KINETICS OF ENHANCED PHOSPHORUS REMOVAL IN THE ACTIVATED SLUDGE PROCESS

by

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DECLARATION BY CANDIDATE

I, Kevan A.C. Martin, hereby declare that this thesis is my own work and that it has not been submitted for a degree of another University.

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SYNOPSIS

An investigation into the removal of phosphorus in the activated sludge process showed that: (1) Luxury uptake of phosphorus may be induced by the presence of an anoxic zone

(2) If a primary and secondary anoxic reactor are present in the system, the actual retention time of the primary anoxic reactor will have the dominant effect on the degree of phosphorus removal.

(3) In a system where only a primary anoxic reactor is present, there is an optimum actual anoxic retention time for obtaining maximum phosphorus removal. This optimum value appears to coincide with the condition where there is no nett release of phosphorus in the anoxic zone. Decreasing or increasing the actual anoxic retention time either side of the optimum value has a detrimental effect on phosphorus removal.

(4) Increasing the influent ammonia - nitrogen and hence the reactor nitrate concentration, enhances phosphorus removal.

(5) An increase in aeration reactor pH to between pH 7-8 enhances phosphorus removal.

(6) The mechanism of removal does not appear to be precipitation. Although an increase in pH through the anoxic reactor was observed due to denitrification, phosphorus was released into solution.

(7) The degree of phosphorus removal is independent of the influent phosphorus concentration.

(8) Anoxic stripping of phosphorus is not a pre-requisite for luxury uptake of phosphorus to occur.

(9) The concentration of phosphorus removed is a function of the COD

utilized. The ratio of phosphorus removed to the COD utilized is constant at a particular sludge age, so that as the concentration of COD utilized increases, the concentration of phosphorus removed increases.

(10) The concentration of phosphorus removed is a function of the sludge age. For a fixed biodegradable influent COD, the longer the sludge age, the less phosphorus removed.

In a configuration where the actual anoxic retention time is fixed, the concentration of phosphorus removed from the effluent may be described by the equation:

$$\Delta P = \frac{Y(S_i - S)}{1 + bR_s}\left[\alpha + 0{,}03(0{,}2bR_s + \frac{1}{0{,}82})\right]$$

Where: ΔP = reduction in phosphorus in the influent total PO_4-P i.e. $(P_{influent} - P_{effluent})$

S_i = biodegradable influent COD (mg/)

S = unmetabolized biodegradable COD in effluent (mg/)

R_s = sludge age (day) defined by $\frac{\text{mass of sludge in reactor}}{\text{mass of sludge wasted/d}}$

Y = growth yield coefficient - mass of organisms synthesized per mass of COD utilized (mg/)

b = endogenous mass loss rate constant (mg VAS/mg VAS/day).

α = the fraction of phosphorus relative to the mixed liquor volatile active suspended solids (MLVASS).

Preliminary investigations into iron chloride addition indicates that iron appears to have disproportionately favourable effect on phosphorus removal under conditions where luxury uptake is taking place.

CONTENTS

INTRODUCTION

Present-day water treatment objectives include the removal of the principal eutrophic elements nitrogen and phosphorus in addition to the classical objectives of stabilisation of oxygen - demanding organic material and removal of suspended solids. Modern activated sludge processes have been developed which are effective in fullfilling all of these objectives excepting the removal of significant amounts of phosphorus. Unlike carbon and nitrogen, influent phosphorus is only removed from the system via the waste sludge. Phosphorus normally constitutes only 2-3% with respect to the MLVSS by mass. Influent phosphorus concentrations usually range from 8-16 mg/ℓ P and approximately 1-3 mg/ℓ P is removed in the sludge wastage. This accounts for only a small fraction of the influent phosphorus.

Certain conventional activated sludge plants have been reported to consistently remove 8-9 mg/ℓ PO_4-P from an influent 10 mg/ℓ PO_4-P. This high removal implies that a far greater mass of phosphorus than normal is being removed via the wasted sludge. Two distinctly different theories have been developed to account for the observed phenomena - the calcium precipitation theory and the luxury uptake theory.

Proponents of the calcium precipitation theory hold that: The maximum mass of phosphorus incorporated in the sludge mass is about 3% by mass of the volatile suspended solids-additional phosphorus appearing in the sludge mass is a result of chemical precipitation of calcium phosphate. The precipitate is captured in the sludge floc and is removed with the waste sludge. Other cations in water such as iron and magnesium have also been implicated in the removal but the effects of these appear to be minor. This mechanism of phosphorus removal can only be effective

in plants treating hard waters with high pH values.

Proponents of the luxury uptake theory hold that:

The mechanism of phosphorus removal is strictly biological - sludge micro-organisms are capable of taking up far more phosphorus than 2-3% with respect to the MLVSS required for growth. The net mass of phosphorus contained in the waste sludge may increase two or three-fold over that necessary for metabolism. Removal takes place in both hard and soft waters.

In South Africa treated effluents are required to be nitrified and denitrified; for this purpose the Barnard denitrification system [22] is being incorporated into many new designs. In pilot plant studies this system has shown significant removal of phosphorus [22]. This makes an investigation into phosphorus removal using the Barnard system or some modification of it most attractive as both phosphorus and nitrogen removal appear to be possible.

The pilot scale plant on which the high phosphorus removal has been observed is located in the Transvaal highveld where the waste waters contain significant concentrations of Ca^{2+} and Mg^{2+} and have a high alkalinity. Investigations of the process with such waters brings in an element of uncertainty as to the mechanism of the phosphorus removal i.e. by luxury uptake of by calcium precipitation. In the Cape Town area the waters are very soft and the possibility of calcium precipitation is remote. Investigations into phosphorus removal using waste waters from the Cape Town area could be both instructive and decisive in deciding between these two theories. In any event a general investigation is merited into the basic conditions leading to phosphorus removal in activated sludge plants.

This report describes the investigations undertaken into phosphorus removal in the activated sludge process. In Chapter 1, the relevant literature is briefly reviewed and the areas requiring investigation are identified. In Chapter 2, preliminary investigations into these areas are reported. In Chapter 3, a kinetic theory for phosphorus removal is proposed. Also, in Chapter 3, some preliminary investigations are reported into improving the performance of the process by the addition of iron salts.

CHAPTER 1 - LITERATURE REVIEW

INTRODUCTION

A number of theories have been proposed to describe the removal of phosphorus from waste water by activated sludge. These are:

Carbon Limitation Theory:

This theory supported by Sawyer[1] Wuhrman[2] and others[3,4] proposes that the amount of carbon available in sewage is the limiting factor in determining the mass of organisms synthesized. The ratio of carbon to phosphorus required for synthesis is given by the ratio of these elements in the bacterial cell composition 106:1. The mass of phosphorus in sewage is usually far in excess of that required for synthesis. Furthermore, the mass of phosphorus that can be removed is only that contained in the mass of sludge waste per day. When a sludge age is imposed on an activated sludge system the phosphorus requirements decrease as the sludge age is increased. In the activated sludge process carbon is oxidised during respiration and lost from the system in the form of carbon dioxide, whereas the phosphorus taken up for cell metabolism is recycled. Thus, according to the carbon limitation theory, only relatively small amounts of phosphorus are removed from the waste water stream.

On occasions plug-flow configuration activated sludge systems have been observed to remove phosphorus in excess of that predicted by the carbon limitation theory. Two other theories have arisen to explain this phenomenon:

Calcium Precipitation Theory:

Proponents of this theory propose that the removal of

phosphorus by activated sludge can occur in two ways - either through sludge synthesis or through cationic precipitation of phosphorus, the precipitate then being removed with the waste sludge.

According to Menar and Jenkins[5], the metabolically produced carbon dioxide (CO_2) determines the pH of the mixed liquor. If the mixed liquor pH is low, the calcium will remain in solution. If enough CO_2 is stripped from the mixed liquor by aeration, the pH will rise to a point where calcium phosphate precipitation occurs. The mass of phosphorus removed is stoichiometrically dependent on the mass of calcium phosphate precipitating. This mechanism of phosphorus removal will thus only be effective in plants treating hard waters

Applying this theory to a conventional activated sludge plant such as at Rilling Road, San Antonio, Texas, the following is assumed to occur: Return sludge and settled sewage enter the head end of the aeration basin. Because of the availability of substrate, the oxygen demand is high, with the result that D.O. concentrations are near zero and dissolved CO_2 concentrations are high. The pH of the mixed liquor is consequently low. As the plug moves down the basin, the substrate concentration diminishes, the oxygen demand drops and less CO_2 is produced. If the rate of aeration is constant, the dissolved oxygen concentration will increase and "blow off" the excess dissolved CO_2. The pH of the mixed liquor then increases to a point where calcium phosphate precipitation will occur. The mass of phosphorus removed by this mechanism is independant of the mass incorporated in the sludge and removed via the waste sludge. Thus the sludge age of the system will have little effect on the removal of phosphorus by this mechanism.

This mechanism is unlikely to operate in activated

sludge processes in areas where the waters are generally soft, for example, water derived from Table Mountain sandstone areas. The municipal waste-waters have a low buffering capacity and low Ca^{2+} content. pH values in the aeration basins can be as low as pH 4,6 in nitrifying activated sludge plants, and rarely rise above pH 7,0 with denitrification. Phosphorus removal by precipitation as $CaHPO_4$ does not readily occur at pH 7 so that removal in excess of that predicted by the carbon limitation theory cannot be described by the calcium precipitation theory. Excess uptake under these conditions may be explained in terms of a biological theory:

Luxury Uptake Theory:

The mechanism of removal is explained in terms of biological incorporation of excess phosphorus in sludge microorganisms. Activated sludge exhibiting such excess phosphorus uptake would have a higher phosphorus content than the 2% - 3% of the MLVSS predicted by the carbon limitation theory.

Proponents of the luxury uptake theory have used the existence of the Krebs metabolic cycle for oxidative phosphorylation as the rationale for the mechanism[6,7,8]. They propose that during oxidative phosphorylation some of the intermediate high energy metabolites formed are shunted into a "reservoir" in the form of polymetaphosphate. This compound, called volutin, normally does not accumulate over long periods. In aging cultures a lack of nitrogen or sulphur apparently hinders the metabolism of volutin and it accumulates in the call[9]. Experiments with 2-4 dinitrophenol[6,7,8] which inhibits oxidative phosphorylation but not substrate phosphorylation, have shown that uptake of phosphorus is also severely inhibited. This would tend to confirm that a biological mechanism is operating.

A major weakness of the theory is that it has only been presented in the qualitative form. No model has yet been devised which allows a quantitative prediction to be made as to the amount of phosphorus removed under specific conditions.

ACTIVE UPTAKE FRACTION IN MIXED LIQUOR

Evidence has been presented by several authors that the sludge is the active agent of mixed liquor in the uptake of phosphorus. In an early study Srihath et al[10] showed that the removal of phosphorus from sewage could be inhibited by heating the sludge to bactericidal temperatures. Classical inhibition experiments[6,7,8,11] using 2-4 dinitrophenol to uncouple oxidative phosphorylation have demonstrated the biological nature of phosphorus removal.

In a significant experiment using sludges from different plants, Bargman et al[12] showed that some property of the sludge itself is important in phosphorus removal. Activated sludge from the Valley Settling Basin, Whittier Narrows, Pomona, and Hyperion plants were aerated with Hyperion primary effluent. Only the Hyperion plant sludge removed from the primary effluent of each of the other three plants. It would appear that the Hyperion sludge is unique in its ability to take up phosphorus. Unfortunately no details are given concerning the composition of the different sludges used.

The work of Yall et al[11] using ^{32}P labelled orthophosphate indicated that the radio-active phosphorus was incorporated into sludge microorganisms under aeration. They reported that the phosphorus removal was governed by a biological mechanism which involved the synthesis of adenosine triphosphate (ATP). Experiments with ^{45}Ca showed that calcium phosphate precipitation occured only to a minor degree. The aerobic heterotrophic bacterial groups, Psuedomonas-Xanthomonas and the

Alcaligenes group appeared to be chiefly responsible for the ^{32}P uptake from the sewage[13]. It is clear from the above observations that sludge is the active uptake fraction in the mixed liquor.

FACTORS INFLUENCING UPTAKE OF PHOSPHORUS BY ACTIVATED SLUDGE.

INTRODUCTION.

While a predictive model has yet to be presented for the luxury uptake theory, many investigators have attempted to determine the conditions necessary for phosphorus uptake. The principal experimental method used has been to aerate return sludge in a flask under various conditions. Although fairly consistent results have been obtained by this batch test method, it nevertheless should be noted that the results obtained are not necessarily applicable to actual activated sludge plants.

Influence of Aeration on Phosphorus Uptake:

Dissolved Oxygen Requirements:

It is generally agreed in the literature that phosphorus uptake only takes place under aerobic conditions[6,7,8,14,15,]. However, there is some disagreement as to the dissolved oxygen concentrations which must be maintained for uptake to occur. According to Brar and Tollefson[7] there is no evidence in the literature for a correlation between dissolved oxygen levels and the uptake of phosphorus. At the San Antonio plant Texas[14], a minimum dissolved oxygen level of 2,0 mg/ℓ was required for effective phosphorus removal. Merely raising the dissolved oxygen concentration above 2 mg/ℓ had no effect on the phosphorus removal. Tests at the Baltimore sewage works[16,17] indicated that phosphorus removal was impaired under oxygen limiting conditions rather than at low oxygen levels per se. Under oxygen limiting conditions carbon removal is

also impaired. Under anoxic conditions, release of phosphorus occurs.

It would appear therefore, that the main effect of high dissolved oxygen concentrations is to reduce the chance of local anoxic conditions occuring and to ensure that the minimum amount of phosphorus is released in the secondary settlers. Thickening of sludge by sedimentation will adversely affect the removal of phosphorus due to the anoxic conditions prevailing.

Aeration rates:

A number of investigators[6,7,8] have observed a correlation between the rate of aeration of a jar of mixed liquor and the amount of phosphorus taken up by the sludge.

Applying various rates of aeration to a batch of 30% return sludge, Levin and Shapiro[6] found that rates of aeration above 17 ml air/sec per 1500 ml sample had little effect on the phosphorus taken up by the sludge. At rates above 17 ml air/sec per 1500 ml sample a maximum uptake of 3,3 mg/ℓ PO_4-P was achieved within two hours. At an aeration rate of 5 ml air/sec per 1500 ml sample the equivalent phosphorus uptake would only have been achieved after three hours aeration. The authors found that a mixed liquor aerated with pure oxygen took up 3,5 mg/ℓ PO_4-P after five hours aeration; a mixed liquor supplied with the equivalent oxygen in air released 0,25 mg/ℓ back into solution.

Brar and Tollefson[7] observed complete phosphorus removal of 11 mg/ℓ PO_4-P with an aeration rate 15,3 ml/sec per 1500 ml sample using a batch of 100% return sludge (MLSS 8300 mg/ℓ). This rate was the maximum value tested. Complete removal was achieved after two hours aeration.

An aeration rate of 7,8 ml air/sec per 1500 ml sample was found by Carberry and Tenney[8] to give a maximum phosphorus removal of 7,0 mg/ℓ PO_4-P within three hours. In this instance the MLSS concentration was approximately 1850 mg/ .

In none of the above studies are details given as to the composition of the sludge or nature of the process from which the sludge is drawn. Factors affecting aeration such as temperature, efficiency of oxygen transfer and dissolved oxygen concentrations are also omitted. Where solids concentrations are given, these are in terms of MLSS which does not give an indication of the active mass of organisms present. No quantitative comparison can be made between the various studies.

On a biological level it is difficult to explain why aeration rate should have an effect on the uptake of phosphorus, unless it merely serves to provide an adequately aerobic well-mixed floc. Merely aerating the mixed liquor at a given rate however, does not ensure that the microorganisms are sufficiently oxygenated as this will depend on the oxygen transfer efficiency. It is probable therefore that similar phosphorus uptake could be achieved with adequate mechanical stirring and lower aeration rates. Optimum aeration rates must remain specific to a particular sludge unless sufficient details are given to allow a quantitative comparison to be made.

Length of Aeration:

In most batch test studies[6,7,8,12,15] phosphorus uptake reaches a maximum value after 2-3 hours aeration. After about four hours continuous aeration slow phosphorus release is observed[6,7,8,9]. According to Brar and Tollefson[7] this is probably a result of endogenous respiration. Wells[15] found that during the first five minutes of aeration the rate of phosphorus uptake in-

creases. Thereafter, as the aeration time increases the rate of uptake progressively decreases. It would appear that the aeration time should be less than four hours for optimum uptake under plug-flow conditions.

Phosphorus Release under Anoxic conditions:

Release of phosphorus from sludge is observed under anoxic conditions[5,6,7,8,9,18]. In a batch test study, Shapiro et al[18] found that the phosphorus release appeared to be controlled by the redox potential level of the mixed liquor rather than by the dissolved oxygen concentration. Randall et al[9] however, reported that under anoxic conditions orthophosphate release occured before any significant change of redox potential. The start of phosphate release was observed to coincide with the occurence of zero dissolved oxygen concentrations. Milbury et al[16] also found that under full scale plant conditions, dissolved oxygen concentrations gave a better indication than redox potential of aeration conditions immediately preceding phosphorus release. Abrupt reductions in dissolved oxygen concentrations in the full-scale system gave rise to reproducable increases in effluent phosphorus concentrations.

There is some uncertainty as to the mechanisms of release however. Release of phosphorus can either occur through bacteriolysis, or through leakage from viable cells. Bacteriolysis is inhibited in the presence of sulphate salts. Brar and Tollefson[7] found that phosphorus release was inhibited by addition of $MgSO_4$ but not by Na_2SO_4. This suggests that cell lysis may not be the mechanism for release. Randall et al[9] observed a similar occurence, with the Na_2SO_4 having little inhibitive effect. The inhibition of phosphorus release was found to be directly related to the amount of $MgSO_4$ added. It is possible that the difference in release may be related to the cation as Mg^{2+} appears to be im-

portant for the formation of volutin. It is noteworthy that the amount of phosphorus taken up by the sludge before release begins was found to be directly proportional to the amount released[9]. This suggests that the bacteriolysis may not be the mechanism of release and that the process may be reversible.

According to Levin and Shapiro[6] an activated sludge with low initial phosphorus content is an important step in achieving the maximum possible uptake of phosphorus by the aerated sludge. Low phosphorus content activated sludge may be created by anoxic release of the phosphorus from the sludge. The rate of desorption of phosphorus under anoxic conditions depends principally on the concentration of organisms present and the temperature. The rate of release increases with increasing MLSS and temperature[18].

The relationship between the anoxic stripping of phosphorus and the uptake of phosphorus under aerobic conditions has not been fully investigated. For example, the Rilling Road plant San Antonio, Texas, and the Hyperion plant Los Angeles are plug-flow type plants experiencing high phosphorus removal of the order of 8-10 mg/ℓ PO_4-P. The only anoxic areas occuring are at the beginning of the aeration tanks and in the secondary settler. Soluble phosphorus profiles along the length of the aeration tank and secondary settlers indicate that desorption of phosphorus from the sludge in the anaerobic areas is minimal. From the data presented it appears that the mechanism of removal is biological and not through chemical precipitation. Desorption of phosphorus from the sludge may not be necessary to the degree which Levin and Shapiro[6] suggest.

Effect of pH:

According to Menar and Jenkins[5] pH is the controlling factor in phosphorus removal in the activated sludge process. Proponents of the luxury uptake theory how-

ever, have found an optimum pH range for phosphorus uptake between pH 7-8[6,7]. At pH values outside this range a diminution in uptake was observed.

Release of phosphorus during aeration has been observed at pH 6,0 by Levin and Shapiro[6] and below pH 5,0 by Wells[15]. The observation that phosphorus is released under low pH conditions has led Levin and Shapiro[6] to suggest acid stripping as an alternative to anaerobic stripping of phosphorus to create a low phosphorus sludge. Levin and Shapiro[6] propose that retaining the sludge for 10 to 20 minutes at pH values between pH 5-6 will be sufficient to induce considerable phosphorus release.

The above observations indicate that in poorly buffered waters nitrification can be detrimental to the phosphorus uptake process. The lowering in pH through the formation of nitric acid may be sufficient to bring about release of phosphorus during aeration. A solution to this problem is to either shorten the sludge age to the point where nitrification does not occur, or to incorporate some form of denitrification in the process.

Effect of Substrate:

If the uptake of phosphorus occurs through the metabolic cycle of oxidative phosphorylation, it may be expected that the addition of a carbon source such as glucose would enhance the uptake. Studies on the effect of adding such a carbon source to sludge under aeration have not given consistent results. Levin and Shapiro[6] found that addition of 1,5 mM/ℓ sodium succinate plus 0,5 mM/ℓ glucose to mixed liquor enhanced the uptake of phosphorus by approximately 2 mg/ℓ PO_4-P after four hours aeration. Carberry and Tenney[8] observed that the addition of monovalent cations such as sodium and pottassium enhanced the uptake of phosphorus. This ob-

servation may explain the results obtained by Levin and Shapiro[6]. Carberry and Tenney[8] found no difference in phosphorus uptake between sludges aerated with different initial dissolved COD values. They concluded that phosphorus removal would not be significantly affected by varying COD concentrations within the range found in typical activated sludge plants.

Data obtained from Brar and Tollefson[7] agrees with those of Levin and Shapiro[6]. In this study 2,5 mg/ℓ D-glucose enhanced the uptake of phosphorus by approximately 1,2 mg/ℓ PO_4-P after four hours aeration. Yall et al[13] used ^{32}P orthophosphate as a marker for the uptake of the phosphorus by the sludge bacteria. Addition of 0,1% glucose to the sewage markedly enhanced the uptake of ^{32}P orthophosphate.

In an attempt to acclimate sludge with poor phosphorus uptake characteristics, Wells[15] aerated sludge in the presence of 200 mg/ℓ glucose and with glucose and 30 mg/ℓ PO_4-P. No improvement in the phosphorus uptake rate was observed after 24 hours of this treatment. Wells[15] also observed no correlation between the phosphorus uptake rate and soluble TOD (total oxygen demand) of the mixed liquor. However, batch test experiments by Randall et al[9] showed a close parallel between the phosphorus uptake and substrate utilization. Both phosphorus uptake and COD stabilization were complete after 7 hours aeration.

All the above data were obtained under batch test conditions. This may give an incorrect impression as to the influence of organic substrate on the phosphorus removal process. Under continuous feed conditions the mass of substrate present determines the mass of organisms synthesized and hence the number of organisms able to take up the phosphorus. It would seem likely that the mixed liquor solids concentration would be significant

in determining the amount of phosphorus removed.

The effect of MLSS Concentration:

Carberry and Tenney[8] have observed no significant difference in the mass of phosphorus taken up by the sludge with MLSS concentrations of 1420;1800 and 2300 mg/ℓ . However, it appears from their data that the maximum possible uptake took place at all MLSS concentrations, with less than 1,0 mg/ℓ PO_4-P remaining in the sludge filtrate in each instance. Different results might have been obtained had the initial phosphorus concentrations been higher. Feng[19] observed good phosphorus uptake with MLSS concentrations below 1500 mg/ℓ with optimum results being obtained at 500 mg/ℓ MLSS with an aeration rate of 560 ml/min/ℓ .

It is apparent from the literature that no optimum MLSS concentration has been found for maximum phosphorus removal. If the luxury uptake mechanism is biological in nature it might be expected that some proportionality exist between the mass of phosphorus taken up and the mass of organisms present. In none of the above studies have the authors reported the process details of the plant from which the sludge was drawn. Thus the composition of the sludge in terms of the active, endogenous and inert fractions cannot be estimated. Furthermore, all the authors have chosen to report the sludge concentrations in terms of MLSS. Kinetic models for activated sludge have shown that the MLVSS concentrations are of use in estimating the active mass of organisms present in sludge[19,20]. The MLVSS/MLSS ratio depends on the particular influent sewage and may vary widely from plant to plant although the mass of organisms present may be the same in each case. The MLSS value does not therefore give a good indication of the active fraction in the sludge. This precludes a quantitative comparison of the results obtained by various authors.

Effect of Sludge Supernatant Phosphorus Concentration:

Surprisingly few authors have investigated the possibility that the sludge supernatant phosphorus concentration may influence the amount of phosphorus taken up by the sludge microorganisms. Brar and Tollefson[7] have found that the lower the initial supernatant phosphorus concentration, the lower is the final concentration after uptake has taken place. The data are too few to conclude, as the authors do, that for a fixed return sludge/primary effluent ratio, the amount of phosphate uptake remains essentially the same.

Randall et al[9] found that the amount of phosphorus taken up tended to vary with the initial supernatant phosphorus concentration though the data are not conclusive. Such a trend might be expected only if the uptake were diffusion controlled. Carberry and Tenney[8] have provided data to show that the sludge microorganisms were able to concentrate phosphorus within the cell against a concentration gradient while uptake was occuring. This apparently involves an active transport mechanism of uptake which would not be dependent on the external phosphorus concentration.

Under anoxic conditions Shapiro et al[18] found the rate of phosphorus release to be constant for a particular solids concentration. According to the authors this suggests that the rate of release is independent of the phosphorus concentration of the sludge supernatant. The phosphorus concentration inside the microorganism is normally much greater than the external medium. Thus the change in supernatant phosphorus concentration under anoxic conditions may only have a slight effect on the rate of release.

Effect of Nitrogen:

As mentioned earlier, volutin accumulation can occur when sources of nitrogen or sulphur are exhausted[9]. Because continuous endogenous respiration occurs in the activated sludge process, it is unlikely that sources of nitrogen are ever depleted sufficiently for this mechanism to operate. Barnard[21,22,23] has however, observed a correlation between low effluent nitrogen values and high phosphorus removal in the Bardenpho nitrification/denitrification process. He has suggested that complete removal of nitrate-nitrogen is an essential prerequisite for high phosphorus removal.

Vacker et al[14] have presented data to show that high phosphorus removals may occur over a wide range of effluent ammonia nitrogen. Furthermore, phosphorus removal was promoted sharply during the initial stages of nitrate formation. According to Vacker et al[14], the extended aeration required for the growth of nitrifying bacteria results in the endogenous destruction of the sludge microorganisms and is consequently detrimental to the phosphorus removal process.

It would seem that, unless the sources of sulphur are severely limited in the same way, metabolic storage of phosphorus is not the result of the depletion of nitrogen or sulphur.

LOCATION OF REMOVED PHOSPHORUS:

An intensive investigation was undertaken by Carberry and Tenney[8] to determine the location of the phosphorus once it had been removed from the sludge supernatant. Phosphorus forming part of the sludge but lying outside the microorganisms was located by washing the solids with a cold 0,85 saline solution. Phosphorus from the soluble fraction of the cells was recovered by extraction with cold 10% trichloroacetic acid. Phosphorus from the insoluble cell fraction was extracted with hot (95°C) 10%

trichloroacetic acid. The remaining biomass was analysed for unextracted phosphorus. The results showed that after phosphorus uptake, the major part of the phosphorus removed from the liquid phase was located in the acid-soluble fraction of the cells. Minor amounts of phosphorus were recovered from the external saline wash, indicating that precipitation was not the mechanism of removal. ^{32}P was used as a tracer in a similar set of experiments to determine that location of phosphorus after its removal from the liquid phase. Again it was found that the major portion of the phosphorus taken up was located in the acid-soluble portion of the cell[8]. Yall et al[13] using ^{32}orthophosphate as a tracer confirmed that a considerable turnover of the phosphorus occurs in sludge.

Experiments on phosphorus release by Shapiro et al[18] indicated two sources of released phosphorus - the acid-soluble fraction and the phosphorus bound in the nucleic acid. The major portion of released phosphorus came from the acid-soluble fraction. Unfortunately no data are presented.

PHOSPHORUS REMOVAL IN ACTIVATED SLUDGE PLANTS:

In a few activated sludge plants, all of plug-flow type configuration using bubble aeration, a high degree of phosphorus removal has been observed. Reports on the influence of various factors on the removal of phosphorus at these plants indicate that the dissolved oxygen concentration in the reactors is perhaps the most important.

At the District of Columbia Sewage Works, plant tests based on batch test data showed that increased aeration of three to four times the normal rate resulted in decreased effluent dissolved phosphorus concentrations[6]. Under normal aeration conditions, anaerobic conditions developed in the midpoint of the aeration basins.

At the effluent end of the basin the dissolved oxygen concentration did not rise above 1,0 mg/ℓ . By substantially increasing the rate of oxygenation, the anoxic and the low dissolved oxygen concentration zones were eliminated, thus reducing the possibility of phosphorus release under anoxic conditions.

An extensive study at the Baltimore Black River Wastewater Treatment Plant[16] into the relationship between dissolved oxygen concentration and high removal of phosphorus gave similar results. When the dissolved oxygen concentration in the aeration tanks fell to low values (0,4 - 0,0 mg/ℓ) release of phosphorus occured. The authors were not able to determine the precise level of dissolved oxygen which triggered phosphorus release. Under normal conditions, where typically high removals of phosphorus are observed almost the entire first half of the aeration tank is anoxic. However, from the data presented it does not appear that the phosphorus release occurs in the first half of the tank. According to the authors, consistently good phosphorus removal could be achieved if the dissolved oxygen concentrations at the effluent end of the aeration tank were maintained above 2,0 mg/ℓ . This would ensure that phosphorus release in the secondary settling tank is kept to a minimum.

Vacker et al[14] have found that while high removal of phosphorus occurs with dissolved oxygen concentrations of about 2,0 mg/ℓ a higher level of aeration at the effluent end of the aeration tank is required to prevent desorption of phosphorus in the secondary settlers. From the batch tests mentioned earlier it would appear that the amount of phosphorus desorped will depend principally upon the solids concentration, the temperature and the retention time of the settling tank. Bunch[24] suggests that the solids retention time in the secondary settler should be less than 30 minutes.

The American practice of using the settling tank as a thickener could have a significant effect on desorption. Return cycle flows are comparatively low, 0,25 - 0,5 of average flow are common, so that the sludge build-up in the tank is high, particularly during the high flow period. In consequence, anaerobic conditions are well developed. In England and South Africa, where nitrification is demanded, the recycle from the settling tank is greatly increased to reduce sludge accumulation and the attendant denitrification effect.

Vacker et al[14] in an extensive analysis of the relationship of various factors to phosphorus removal at San Antonio Sewage Works report that a "reverse" taper effect was the result of partially clogged diffusers in the front quarter to half length of the aeration tanks. From the few data presented it does not appear that anoxic conditions occured at all in the aeration tank. Experiments comparing the effects of tapered and "reverse" tapered aeration on the West Road plant San Antonio showed that the pattern of air distribution had little effect on the phosphorus removal if dissolved oxygen concentrations did not fall below 2,0 mg/ℓ for most of the length of the aeration tank.

At the Rilling Road plant a high removal of approximately 8 mg/ℓ PO_4-P consistently occurs[14]. A significant positive correlation of mixed liquor solids and effluent nitrate nitrogen with percent phosphorus removal was observed. A significant negative correlation of percent phosphorus removal with the effluent BOD, effluent suspended solids, effluent ammonia nitrogen and BOD loading was observed. It should be noted, however, that the percent phosphorus removal depends on the influent phosphorus concentrations and not on the mass of phosphorus removed. Thus while two processes may remove the same mass of phosphorus their percent phosphorus removals may be different.

Menar and Jenkins[5] established a pilot plant at San Ramon California which matched the Rilling Road plant conditions, with the exception that the mixed liquor dissolved oxygen concentrations and pH values at San Ramon were higher at the influent end of the plant. Under these conditions only 3 mg/ℓ PO_4-P was removed in the pilot plant compared to 9,6 mg/ℓ PO_4-P at Rilling Road. From this result they concluded that the factors reported by Vacker et al[14] were of no significance to the phosphorus removal process. Menar and Jenkins[5] offer no explanation for the marked discrepancy in phosphorus removal under seemingly identical conditions.

Experiments on the Hyperion treatment plant Los Angeles, based on the Menar and Jenkins pilot plant model, showed that phosphorus removal in the plant could be accounted for by cationic precipitation of phosphate, if certain reactions were assumed[12]. A stoichiometric balance between the phosphate anion and the cations of calcium, aluminium, zinc and iron could be achieved. Data obtained along the length of one aeration tank during a period of high phosphorus removal showed a progressive decrease in soluble phosphate concentration and a progressive increase in nitrate-nitrogen and pH. Removal of soluble phosphorus is complete after 6,6 hours aeration. No release of phosphorus in a secondary settlers after five hours retention was observed. Unfortunately no dissolved oxygen profiles are presented.

A further experiment comparing the effect of step aeration vs. plug-flow conditions was conducted[12]. As primary effluent was added to the mixed liquor under the step-flow regime, the soluble phosphorus concentration increased sharply at each step addition and then returned to near zero after one hour's aeration. The nitrate nitrogen and pH dropped initially but returned to their former levels, or higher, after one hour's

aeration. It would seem that under the extreme condition of a completely mixed regime, some residual phosphorus would inevitably appear in the effluent.

Other experiments at the Hyperion plant[12] indicated that some particular characteristics of the Hyperion sludge are important for the observed removal of soluble phosphorus. Although the Menar and Jenkins hypothesis[5] can account for the removal, some other mechanism may be operating.

Levin et al[25] have designed and operated a system for phosphorus removal based on data obtained from laboratory experiments. In this system an anaerobic zone is introduced between the secondary settling tank and the inlet end of a plug-flow aeration basin. The return sludge passes into this anaerobic zone and is gently stirred for 4-6 hours to strip the phosphorus from the sludge. The small volume of supernatant liquid is treated with lime to precipitate the stripped phosphorus. In addition to removing phosphorus through the waste sludge, phosphorus is also removed by precipitation. The stripped sludge is returned to the aerobic reactor for further uptake of phosphorus. The mechanism for phosphorus removal is therefore not solely biological.

All the above observations were made at plug-flow plants with short sludge ages. It is of interest to note that Barnard[21,22,23] has observed high phosphorus removals in a completely mixed extended aeration plant designed for complete biological denitrification. This plant consisted of a multi basin system where the influent sewage was fed into an anoxic zone , which was followed by an aeration zone, another anoxic zone and a reaeration zone before settling. According to Barnard[21,22] high phosphorus removal could only be obtained when complete denitrification occured. The pH of the reaeration zone did not appear to be the major factor in the

removal. Similar results were observed in a laboratory scale model[21]. Unfortunately no further details of the operating conditions of the plant are given.

CONCLUSIONS

It is clear from the literature survey that no general conclusions may be drawn as to the conditions required for phosphorus removal. It would appear that under conditions where the Menar and Jenkins hypothesis of calcium precipitation does not apply, a well-oxygenated sludge is necessary. This is not the sole requirement for achieving high phosphorus removal, but no other single factor is generally agreed upon to be necessary. A plug-flow regime, while apparently the optimum configuration for high removal of phosphorus is not in itself a necessary condition for high removal. This has been shown by the work of Bargman et al[12], mentioned above.

A factor of particular relevance to South African conditions is that of the presence of nitrates. According to Barnard[21], complete removal of nitrates is a necessary precondition for high removal of phosphorus. The high removal of phosphorus observed under low nitrate conditions cannot be due to a nitrogen limiting condition enhancing the metabolic production of polymetaphosphates. High phosphorus removal is observed in activated sludge plants where nitrification does not occur and TKN values are high. Bargman et al[12] observed effluent nitrate-nitrogen concentrations of over 5 mg/ℓ NO_3-N during periods of high phosphorus removal at the Hyperion plant. This suggests that the prerequisite of removal of nitrates advocated by Barnard[21,22] may be peculiar to the Bardenpho process.

A major drawback in all the studies cited is the practice of measuring the MLSS concentration and not the MLVSS concentration of the sludge, and lack of details of the

process from which the sludge is drawn. To the writer's knowledge, no studies reported have attempted to relate the active mass of the sludge to the mass of phosphorus removed under given conditions. Unless this is done, different studies will only be comparable on a qualitative level. At present no estimate can be made as to the relative efficiencies of many of the processes reported in the literature.

A degree of uncertainty exists as to the role of the influent COD in the phosphorus removal process. According to Wells[15] and Vacker[14] tha mass of phosphorus removed through the waste sludge will depend on the mass of solids produced. If the influent is of low strength, insufficient solids will be produced to allow adequate phosphorus removal. In contrast Carberry and Tenney[8] maintain that impairment of phosphorus removal will only occur if the influent concentration is significantly lower than that found in normal plants so that within certain limits, the removal of phosphorus is relatively independant of the influent COD.

One factor which has not been adequately investigated, is the influence of an anaerobic or anoxic zone on the removal of phosphorus. In all batch test studies it is likely that the sludge tested would have been anaerobic or anoxic for some period before testing. Most of the reported studies used return sludge as the sample which would thus have been anoxic for some period in the secondary settling tank.

Levin and Shapiro[6] have found that stripping phosphorus from the sludge under anaerobic conditions leads to enhanced removal of soluble phosphorus. In most plant studies, the dissolved oxygen levels are low or zero at the influent end of the aeration tank. Unless the mixing is very good it is likely that at least part of the return sludge is anoxic for a period in the initial

stage of the plug-flow system. In the Barnard system, the reaeration basin is preceded by an anoxic basin of about two hours retention time. It is possible therefore that an anoxic stage is necessary for high removal of phosphorus.

SCOPE OF INVESTIGATION:

In this investigation an anaerobic/anoxic zone preceding an aeration zone was proposed as a necessary prerequisite for biological phosphorus uptake. The first objective of this investigation was to test, at least qualitatively if this hypothesis has any validity. The first experimental work did lend support to this hypothesis so that in subsequent investigations anoxic zones formed an integral part of the process. The problem then devolved into determining the conditions required for optimal phosphorus removal. To this end the influence of the following factors on phosphorus removal were investigated:

(i) Length of anoxic and aerobic retention
(ii) Nitrate - nitrogen concentration
(iii) pH
(iv) Influent phosphorus concentration
(v) Influent COD
(vi) Sludge age

These factors were all tested to that degree where their significance or otherwise became apparent. The conclusion from this initial investigation was that the primary anoxic zone, which receives the influent and the recycled sludge underflow was the main process condition influencing phosphorus removal. This led to a more detailed investigation of the influence of the anoxic retention time and the return sludge recycle ratio on phosphorus removal.

It was recognised however, that the process of phosphorus

removal occurs in two stages: (i) incorporation of phosphorus into the sludge (ii) removal of the sludge from the system. The importance of the second stage has gone virtually unrecognised in the literature and to the authors knowledge has not been experimentally investigated.

The mass of sludge wasted per day depends on the sludge age of the plant. It is known however, that activated sludge consists of at least three fractions - the active, the endogenous and inert fractions. From the work of Carberry and Tenney[8] it is evident that it is the active fraction that is responsible for the uptake of soluble phosphorus. Thus the fractions present in sludge do not all contain the same portions of phosphorus. Under the wide range of loading conditions encountered, it is only by means of a kinetic theory of the activated sludge process that it is possible to estimate the fractions of sludge present and hence the mass of phosphorus absorbed by the active fraction. Once the active mass present is known, some prediction as to the mass of phosphorus removal can be made. The use of the kinetic theory is therefore a key step towards a predictive model of phosphorus removal.

The third part of the investigation constitutes the development of a kinetic model of phosphorus removal, and an experimental investigation into the predictive implications value of the model. Finally, having established a model, an investigation was conducted into further enhancing the phosphorus removal by chemical addition of iron salts. Here the objective was <u>not</u> to investigate stoichiometric effects of the iron combining with the phosphorus but to investigate if the biological process of phosphorus removal could be assisted by small additions of coagulating salts. This aspect was considered important for it was observed[26,27] that the Scottburgh activated sludge plant in Natal continued removing phosphorus for a period after the addition of iron and aluminium salts had been terminated.

CHAPTER 2 PRELIMINARY INVESTIGATIONS

INTRODUCTION:

In the preliminary investigations no attempt was made to exhaustively test the effect of the various factors on phosphorus removal. It was felt that if any factor was of major influence, its effect would soon become readily apparent, at which point it could be more closely investigated.

APPARATUS AND METHODS:

All laboratory scale units were constructed of perspex to the size required for the particular experiments. (e.g. Fig. 1 and Fig. 2). The contents of all reactors were stirred with motor driven paddles to ensure complete mixing. The anoxic reactors were totally enclosed, the paddle shaft passing through an air tight bearing in the lid. The settling tank was designed to allow a minimum solids retention time (Fig.2.). The mixed liquor was both introduced and withdrawn at the bottom of the settling tank. Since the solids/liquid interface was only slightly above the outlet port, the solids retention time may be regarded as minimal at the recycle ratios used. Dissolved oxygen concentrations at the bottom of the settler were usually above zero. Under these conditions desorption of phosphorus in the settler did not occur. Aeration was by means of valve-regulated bubble diffusers. Except when otherwise stated dissolved oxygen concentrations were maintained between 1-2 mg/ℓ measured by means of a Yellow Springs oxygen probe. All experiments were conducted in an air-conditioned laboratory at 20°C.

Unsettled sewage was used throughout the investigation. Influent was collected from the Zeekoevlei sewage works every 1-2 weeks, macerated and stored at 4°C in stainless steel 200ℓ tanks. After dilution to the required

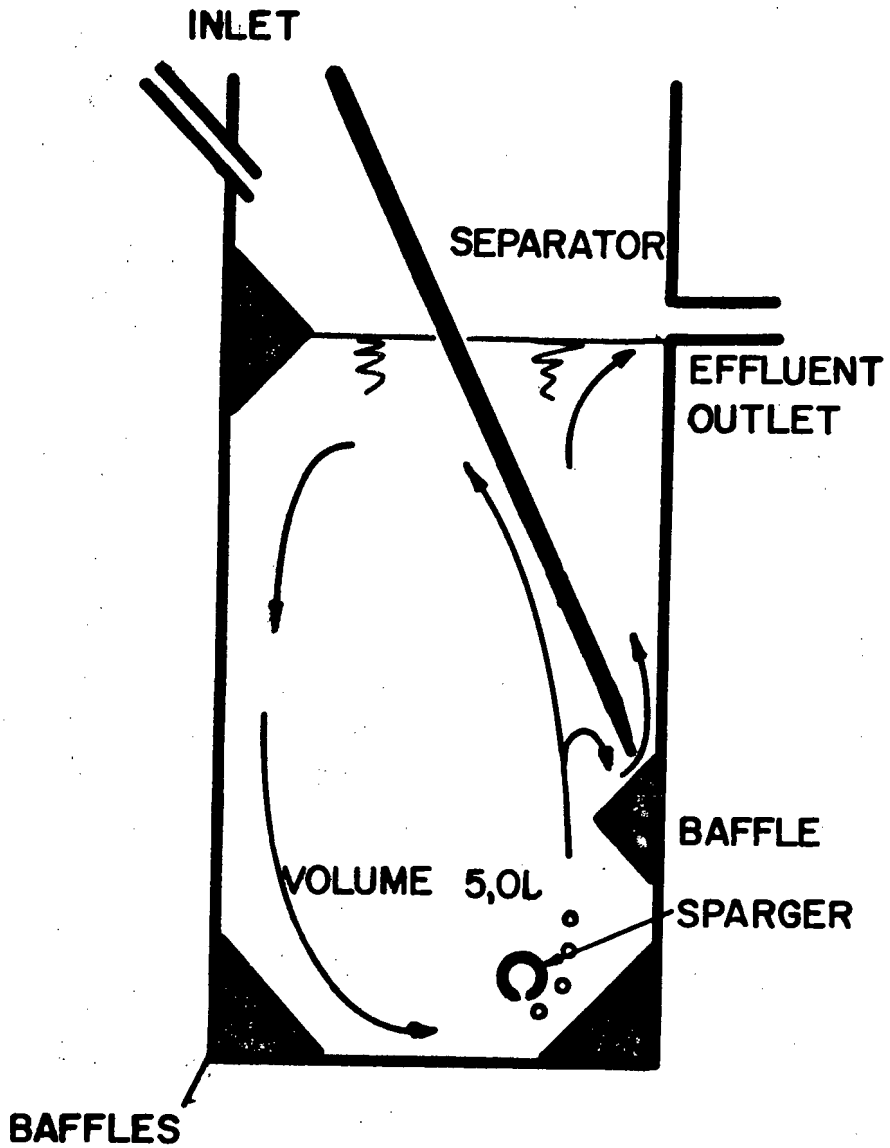


Fig. 1. Completely aerobic activated sludge unit.

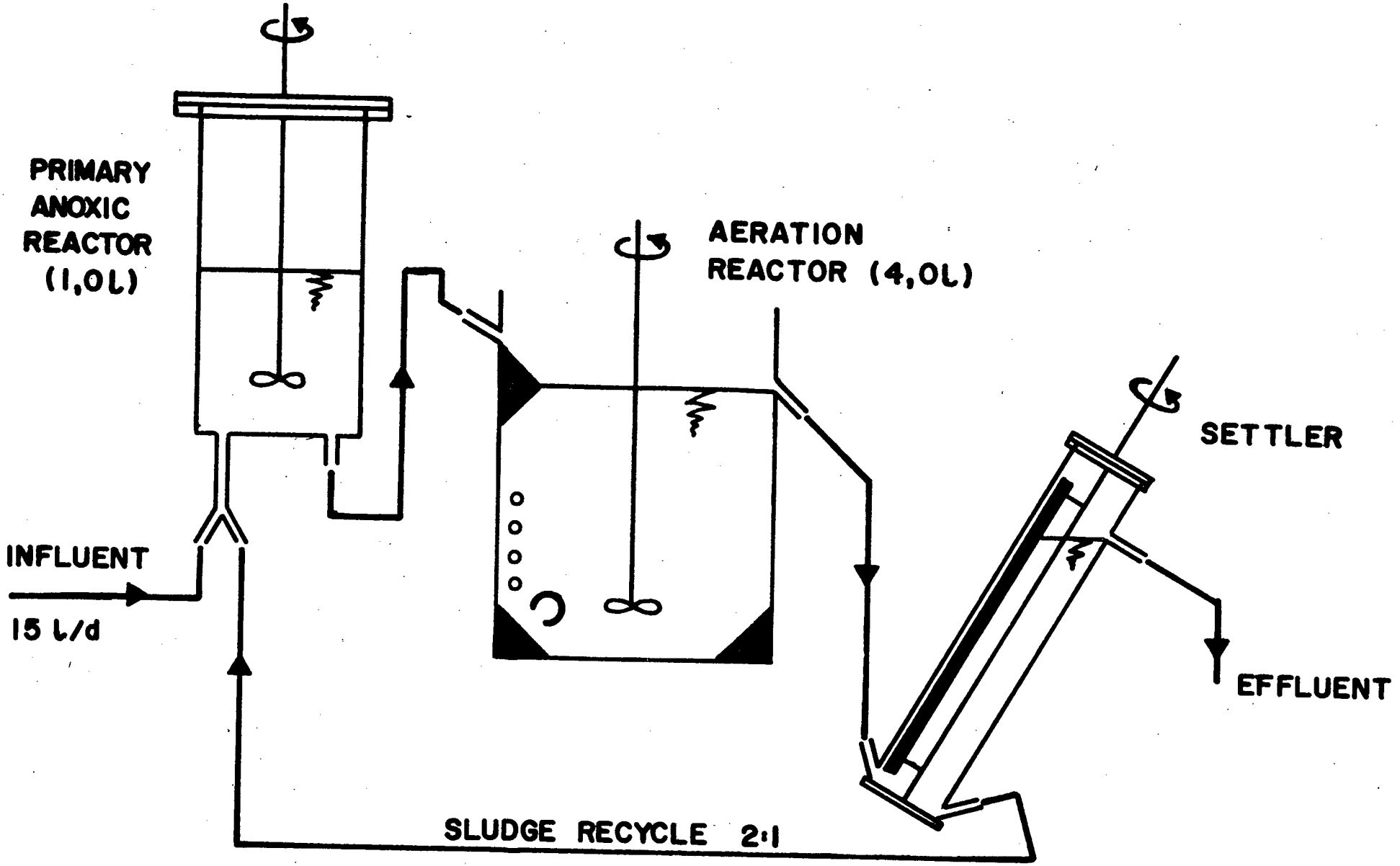


Fig. 2. Activated sludge unit with seperate settler, primary anoxic reactor and aeration reactor.

strength, the daily quantity of feed was sampled and transferred to a clean plastic container kept at 4°C. The feed was gently stirred to prevent settling of the sewage particles. The influent feed and recycle ratio flow rates were regulated by means of peristaltic pumps (Scientific Mnf. Co., Cape Town). Effluent was collected in a clean plastic bucket.

The units were fed between 11 a.m.-12 p.m. daily. The required mixed liquor samples were taken at 8 a.m. Immediately a sample was taken it was vacuum filtered through Whatmanns No. 1 filter paper. All samples were tested on the day of sampling. The methods for measuring COD, TKN and MLVSS are those described in "Standard Methods"[29]. The pH was measured within 0,1 pH units with a pH meter (Radiometer type 29). NO_3-N and NO_2-N concentrations were analysed by a Technicon Auto-analyser according to the Technicon Auto-analyser Methodology. Total phosphorus concentrations were measured using the technique described in Appendix 1. The results are reported as total PO_4-P (mg/ℓ).

ANOXIC INDUCTION OF ENHANCED PHOSPHORUS REMOVAL

The initial hypothesis - that an anaerobic/anoxic zone preceeding an aerobic zone is a necessary pre-requisite for excess phosphorus removal - was tested as follows: A laboratory scale completely mixed activated sludge (CMAS) unit was set up and a sludge age of 10 days established. The unit used was identical to that designed by Marais[19] see Fig. 1. This design has the advantage that while good sludge-liquid separation is achieved, the sludge in the seperator does not become anaerobic. Dissolved oxygen concentrations in the reactor were maintained at 6,0 mg/ℓ to ensure a fully aerobic well mixed floc and to prevent dissolved oxygen concentrations in the separator falling below 3,0 mg/ℓ . The sludge was thus constantly aerobic. When sufficient data had been obtained, the reactor was divided into an aerobic and an anaerobic reactor (Fig.2.). The total

volume of the system remained unchanged. Sludge was recycled from a separate settler to the anoxic reactor where it was mixed with the influent before passing into the aerobic reactor. The results are given in Table 1a and 1b.

On adding the anoxic reactor to the completely aerobic unit, the phosphorus removal from the system increased from 3,0 to 7,4 mg/ℓ total PO_4-P. After running the unit for two sludge ages (20 days) and obtaining consistently high removal, the anoxic reactor was removed from the configuration. The completely aerobic system was re-established (Fig.1.). On removing the anoxic reactor a precipitous drop in the concentration of phosphorus removed was observed. Consistently low levels of phosphorus removal were obtained (Table 1c).

Table 1(a)	Completely Aerobic	
Parameter (mean values)	Influent	Aeration/ Settler
Total PO_4-P (mg/ℓ)	9,7	6,7
COD "	395	78
Phosphorus removed = 3,0 mg/ℓ total PO_4-P		

Table 1(b)	With added anoxic reactor		
Parameter (means values)	Influent	Primary Anoxic	Aeration/ Settler
Total PO_4-P (mg/ℓ)	11,9	3,6	4,5
NO_3-N "		5,7	7,9
NO_2-N "		<0,2	<0,2
MLVSS "			2033
TKN "	29,7		3,4
pH		7,3	7,0
Phosphorus removed = 7,4 mg/ℓ total PO_4-P			

Table 1(c)	Completely aerobic	
Parameter (mean values)	Influent	Aeration/ Settler
Total PO_4-P (mg/ℓ)	8,3	4,9
NO_3-N "		8,0
NO_2-N "		<0,2
MLVSS "		2399
TKN "	21,3	2,7
Phosphorus removed = 3,4 mg/ℓ total PO_4-P		

Table 1(a),(b),(c). Phosphorus removal under completely aerobic conditions and with an added anoxic reactor.

These experiments verified the hypothesis that the presence of an anoxic zone in the system may have significant effect on the amount of phosphorus removed.

Once it had been established that luxury uptake of phosphorus may be induced by the presence of an anoxic zone, it was necessary to determine the most effective configuration. The Barnard process (Fig. 3.) includes anaerobic/anoxic zones and could serve as a starting point for the investigation. However, it is a complex system in which a number of variables are present. Changing one variable often directly influences another. For this reason simpler systems were devised in which it was possible to isolate in a more positive manner the different aspects of the system.

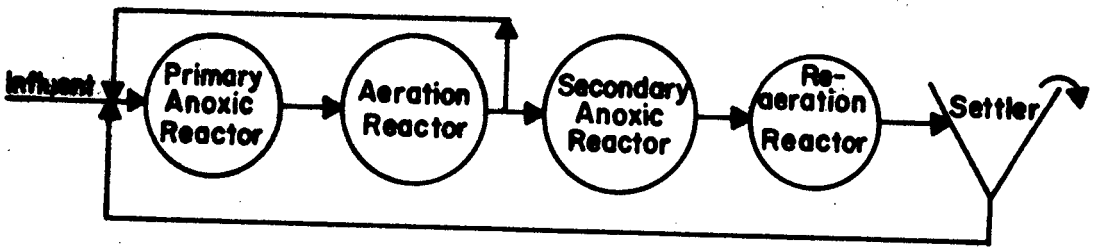
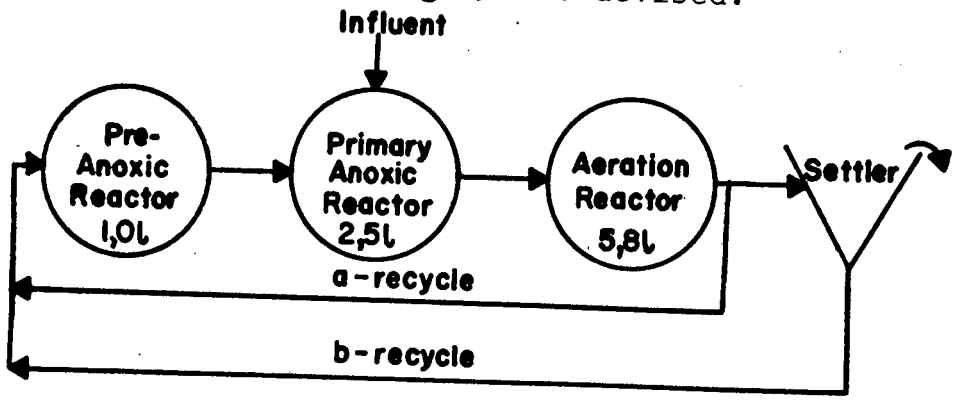


Fig. 3. The Barnard nitrification-denitrification process.

INFLUENCE OF PRIMARY AND SECONDARY ANOXIC RETENTION TIME

Barnard stated that a deep anoxic region was a pre-requisite for good phosphorus removal[23]. To test this hypothesis the system in Fig.4. was devised.



Sludge Age = 15 days Temperature = 20°C

Influent flow = 25 ℓ/d. Recycle ratios a = 2, b = 1

Reactors	Normal retention times (hrs)	Actual retention times (mins)
Pre-anoxic	0,96	19
Primary anoxic	2,40	36
Aeration	5,56	83

Fig. 4. Modified Barnard configuration with process data.

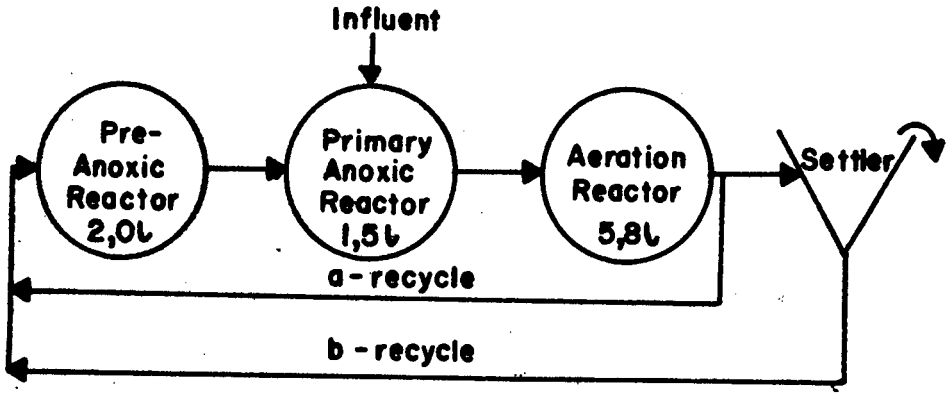
The configuration shown in Fig. 4. allows maximum reduction of nitrate-nitrogen in the pre-anoxic reactor i.e. it induces maximum anoxic conditions before the raw sewage is added in the "primary" anoxic or anaerobic reactor. The relevant data are given in Table 2.

Parameter (mean values)	Influent	Primary Anoxic	Pre-Anoxic	Aeration/ Settler
Total PO_4-P (mg/ℓ)	15,7	7,9	9,2	8,9
NO_3-N "	<0,2	1,6	6,5	7,9
NO_2-N "		<0,2	<0,2	<0,2
MLVSS "				4195
TKN "	54,6			12,7
COD "	660			47
pH		7,5		7,0
Phosphorus removed = 6,8 mg/ℓ total PO_4-P				

Table. 2: Data from Modified Barnard process.

From Table. 2. the mean removal of phosphorus was 6,8 mg/ℓ total PO_4-P. A mass balance gave the fraction of phosphorus relative to the MLVSS as 4,9% which indicates enhanced removal of phosphorus when compared to the usual 2-3% in conventional activated sludge plants. Vacker et al[14] have observed fractions of phosphorus relative to the MLVSS of up to 7%. Optimum conditions had thus not been attained.

As the actual retention time in the primary anoxic reactor was longer than required for optimum denitrification in terms of the denitrification kinetic theory[31], the volume of this reactor was reduced from 2,5 ℓ to 1,5 ℓ . This reduced the retention time from 36 minutes to 22 minutes. At the same time, the pre-anoxic reactor volume was increased by an equivalent volume to maintain approximately constant total actual and anoxic retention times (see Fig. 4a). All other parameters were held constant.

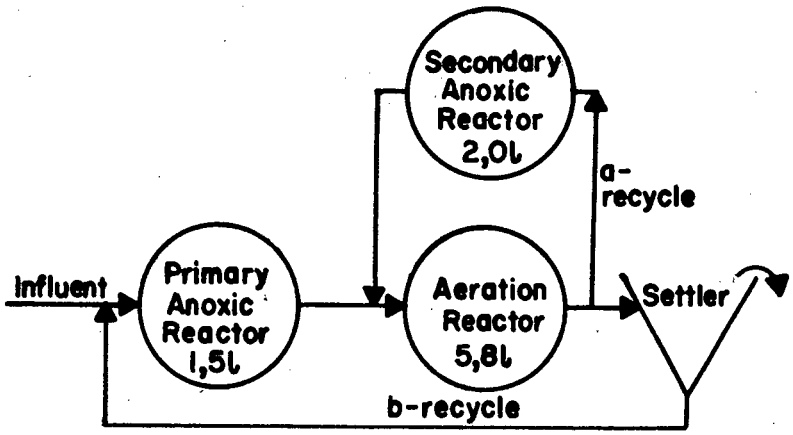


Sludge age = 15 days
Influent flow = 25ℓ/d
Temperature = 20°C
Recycle ratios: a = 2; b = 1

Reactors	Nominal retention time (hrs)	Actual retention time (mins)
Pre-anoxic	1,92	38
Primary anoxic	1,44	22
Aeration	5,56	83

Fig. 4a. Modified Barnard system with altered relative anoxic retention times. Process data as given.

The mean removal achieved after this change was 6,9 mg/ℓ total PO_4-P i.e. no significant change from the previous configuration. It was concluded that the relative retention times of the two anoxic reactors apparently had no effect on the phosphorus removal. However it was still possible that the actual anoxic retention times or the actual aeration time may have some effect on phosphorus removal. A preliminary investigation into these factors was then undertaken. For this series of experiments one modification was made to the configuration shown in Fig. 4a. The modification involved returning the outflow from the pre-anoxic reactor to the aeration reactor instead of the primary anoxic reactor. The pre-anoxic reactor thus became a separate secondary anoxic reactor (Fig. 5.).



Sludge Age = 15 days Temperature = 20°C
Influent flow = 18,75 ℓ/d

Reactors	Nominal retention times (hrs)
Primary anoxic	1,92
Secondary anoxic	2,56
Aeration	7,42

Fig. 5. Denitrification unit with seperate primary and secondary anoxic reators.

This alteration was considered desirable for the following reasons:

(i) The retention times of the anoxic reactors could be varied individually by altering the particular recycle ratio

(ii) The individual effects of the two anoxic reactors could be seperated without removing either from the system. (Removing either would require making a number of un-desirable compensatory changes as well as altering the denitrification characteristics of the system)

(iii) A constant actual aeration time could still be maintained even if the anoxic retention times were altered by changing the recycle ratios.

In order to determine the principal effects of the actual retention times of the various reactors, the following set of experiments was devised:

(A) An initial condition would be established

(B) The retention times of the primary and secondary anoxic reactors would then be changed but the aeration time would be held constant. If any change in phosphorus removal were observed it could then be ascribed to some condition in the actual anoxic retention times.

(C) If a change in removal occured the retention time of one of the anoxic reactors would be altered to determine which anoxic reactor was responsible. This alteration in anoxic retention time would also alter the aeration reactor retention times. If no change in removal occured after (B), the actual anoxic retention times would then not be of significant influence in phosphorus removal. The change in (C) would then show if the actual aeration time was of any significance.

It was thought that the above experiments would give some pointers as to the direction of further investigations.

(a) The initial condition was established with the a recycle = 2 and the b recycle = 1. Under this condition the phosphorus removal obtained was 8,8 mg/ℓ total PO_4-P (Table 3(a)).

(b) The retention times of the primary and secondary anoxic reactors were altered by changing the a recycle to 1 and b recycle to 2. The actual aeration time remained constant. An increase in phosphorus removal from 8,8 mg/ℓ total PO_4-P to 11,4 mg/ℓ total PO_4-P was observed after making this change (Table 3(b)). This indicated that the actual anoxic retention times had some influence on phosphorus removal and suggested that the actual

Recycle ratio a = 2 b = 1				
Table 3(a).	Inf.	Primary Anoxic	Secondary Anoxic	Aeration/ Settler
Actual retention time (mins)		52	78	105
Total PO_4-P (mg/ℓ)	14,8	9,9	8,7	6,0
NO_3-N "	<0,2	1,5	4,6	8,5
MLVSS "				3355
TKN "	29,5			7,5
COD "	574			56
pH		6,8		6,6
Phosphorus removed = 8,8 mg/ℓ total PO_4-P				

Recycle ratio a = 1 b = 2				
Table 3(b)	Inf.	Primary Anoxic	Secondary Anoxic	Aeration/ Settler
Actual retention time (mins)		38	156	105
Total PO_4-P (mg/ℓ)	17,4	9,2	6,5	6,0
NO_3-N "		0,5	0,5	5,1
MLVSS "				3388
TKN "	35,7			5,2
COD "	633			32
pH		7,6	7,5	7,5
Phosphorus removed = 11,4 mg/ℓ total PO_4-P				

Recycle ratio a = 1 b = 4				
Table 3(c)	Inf.	Primary Anoxic	Secondary Anoxic	Aeration/ Settler
Actual retention time (mins)		29	156	70
Total PO_4-P (mg/ℓ)	20,2	8,9	6,7	7,0
NO_3-N "		13,6	17,7	23,3
MLVSS "				3263
TKN "	68,8			2,4
COD "	586			83
pH		7,5	7,4	7,4
Phosphorus removed = 13,5 mg/ℓ total PO_4-P				

Table.3(a),(b),(c): Phosphorus removal under varying conditions of actual anoxic and aerobic retention times.

aeration time was not significant.

(c) The primary anoxic retention time was reduced by increasing b recycle ratio to 4. This reduced the primary anoxic retention time from 38 mins to 29 mins and reduced the actual aeration time from 105 minutes to 70 minutes. The secondary anoxic reactor retention time was held constant.

(d) Again an increase in phosphorus removal from 11,4 to 13,2 mg/ℓ total PO_4-P was observed (Table 3(c). This occured even though the actual aeration time was reduced and supports the conclusion made in (b). The secondary anoxic reactor actual retention time was thus of little influence. It appeared therefore, that the progressive increase in phosphorus removal observed was principally due to progressive decrease in the primary anoxic reactor actual retention time through the steps (a) to (c).

To summarise, the preliminary conclusions from these series of experiments were:

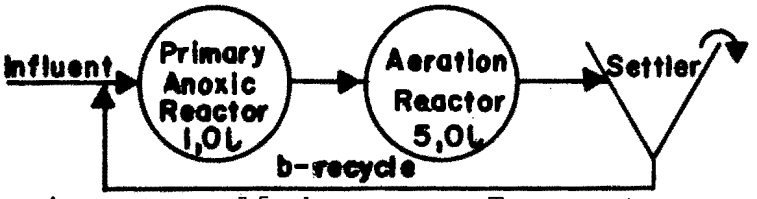
1. The primary anoxic reactor retention is the significant factor in inducing conditions for phosphorus removal. Neither the secondary anoxic retention time nor the aeration retention time appear to be significant in the configuration tested (Fig. 5).
2. The efficiency of removal appears to increase as the actual anoxic retention time of the primary anoxic reactor is reduced by increasing the recycle ratio.

As the secondary anoxic reactor did not appear to be a significant factor in inducing conditions favourable for enhanced phosphorus removal, the main thrust of this investigation was oriented towards assessing phosphorus removal as effected by the primary anoxic reactor only under different conditions. However, a number of secondary investigations were performed concurrently with the above investigation so that these are reported for

configurations which include the secondary anoxic reactor as in Fig. 5, although it is recognised that this configuration is not the best for optimum phosphorus removal.

THE INFLUENCE OF THE ACTUAL PRIMARY ANOXIC REACTOR RETENTION TIME

In the literature it is generally reported that under anoxic conditions release of phosphorus occurs[16,18]. On certain occasions during this investigation however, release did not occur. In the configuration shown in Fig. 6, the soluble phosphorus levels in the anoxic reactor were found to be consistently lower than those in the aerobic reactor (see Table 4.) The actual retention time in the primary anoxic reactor was short - 25 minutes - and phosphorus was actually removed from solution in the reactor. Furthermore, good removal of phosphorus did occur in the system. These observations suggest that long anoxic retention times with consequent phosphorus "stripping" are unnecessary to induce luxury uptake of phosphorus. This raises the question as to what conditions in the primary anoxic reactor give rise to the optimum removal of phosphorus from the system.



Sludge Age = 15 days Temperature = 20°C
Influent flow = 19 ℓ/d b recycle ratio = 2

Reactor	Nominal retention time (hrs)	Actual retention time (mins)
Primary anoxic	1,26	25
Aeration	6,31	126

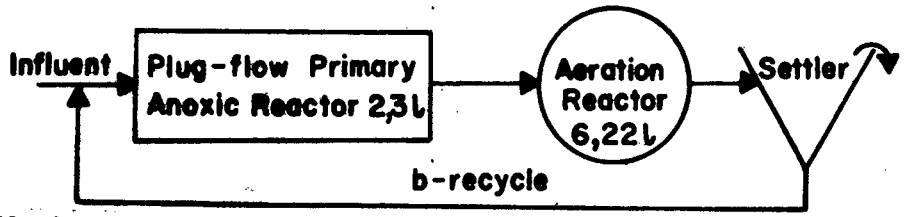
Fig 6. Configuration and process data of unit with lower soluble phosphorus levels in the primary anoxic reactor than in the aeration reactor.

Parameter (mean values)	Influent	Primary Anoxic	Aeration/ Settler
Total PO_4-P (mg/ℓ)	16,6	5,5	6,0
NO_3-N "		5,3	14,4
MLVSS "			5172
TKN "	50,1		7,4
COD "	531		56
pH		7,1	6,7
Phosphorus removed = 10,6 mg/ℓ total PO_4-P			

Table 4. Data obtained from unit showing consistently lower soluble phosphorus levels in the primary anoxic reactor than in the aeration reactor.

Investigation using a Plug-Flow Primary Anoxic Reactor

An intensive investigation was undertaken in the UCT laboratory by M. Marsden[30] on the rôle played by the primary anoxic reactor in phosphorus removal. A unit consisting of a plug-flow anoxic reactor and an aerobic reactor (Fig. 7), was maintained at a constant sludge age of 20 days and received an influent COD of 550 mg/ℓ . The actual anoxic retention time could be altered either by changing the return sludge recycle ratio or by reducing the anoxic plug-flow reactor volume. These two parameters were varied independently to establish the effect of the actual anoxic retention time and the influent/return sludge ratio on phosphorus removal. The process data are given in Fig. 7 and the results are shown in Figs. 8 & 9.



Sludge Age = 20 days Temperature = 20°C
Influent flow = 16 ℓ/d
Nominal retention time (hrs)
Primary anoxic reactor = 3,45
Aeration reactor = 9,33

Fig. 7. Configuration and process data of the unit used by Marsden[30] with plug-flow primary anoxic reactor.

From Fig. 8 it would appear that the optimum uptake of phosphorus is dependent principally upon the actual anoxic retention time and not the influent/return sludge ratio. The maximum phosphorus removal from the system occured at an actual anoxic retention time of 30 minutes (Fig. 9). This point of maximum removal coincides with the point of zero nett release of phosphorus in the anoxic reactor (Fig. 8). This confirms the observation made in the previous section that the concept that phosphorus must be "stripped" from the sludge to improve phosphorus uptake during reaeration appears to be incorrect. However, a minimum actual anoxic retention time is necessary before the maximum system removal of phosphorus occurs (Fig. 9).

It is also noteworthy that at actual anoxic retention times below 30 minutes nett removal of phosphorus was observed in the anoxic zone. Marsden notes that the initial removal of phosphorus in the anoxic plug-flow coincides with the rapid denitrification phase[31]. He suggests that this initial removal of phosphorus may be part of a general rapid absorption phase which could mask the initial release of phosphorus under anoxic conditions.

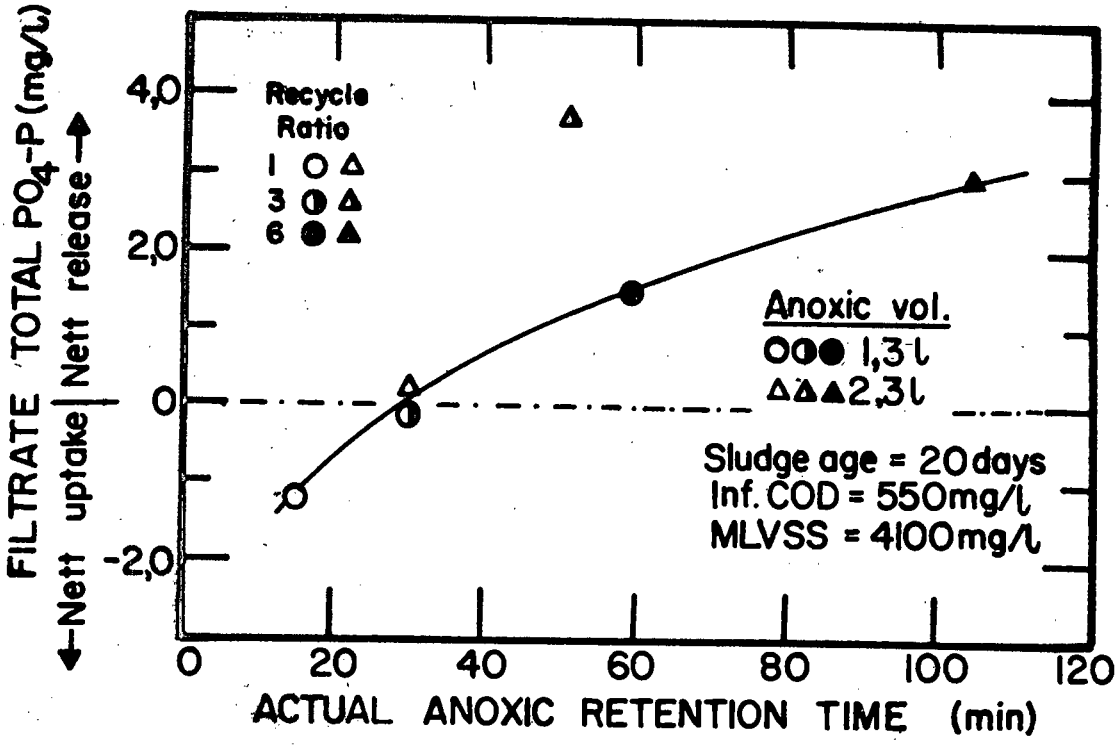


Fig. 8. Nett change in filtrate total PO_4-P concentration in a plug-flow anoxic reactor at various actual anoxic retention times.

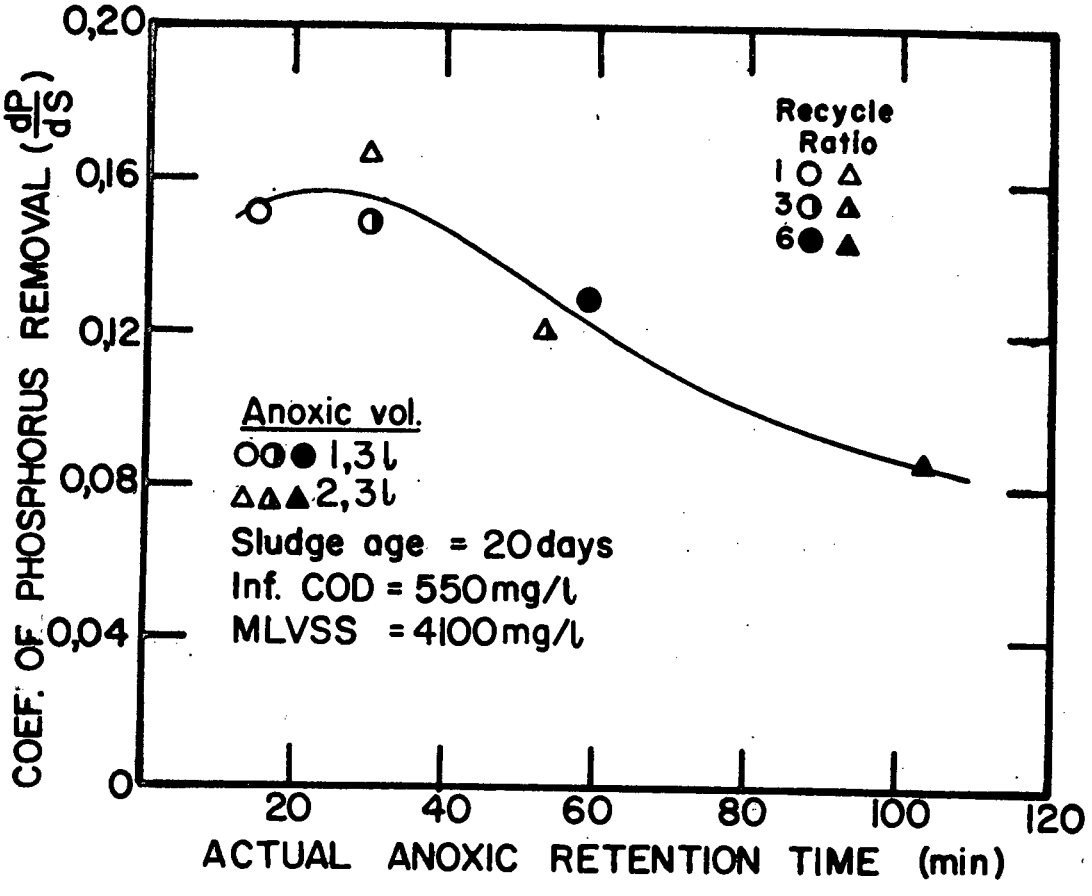
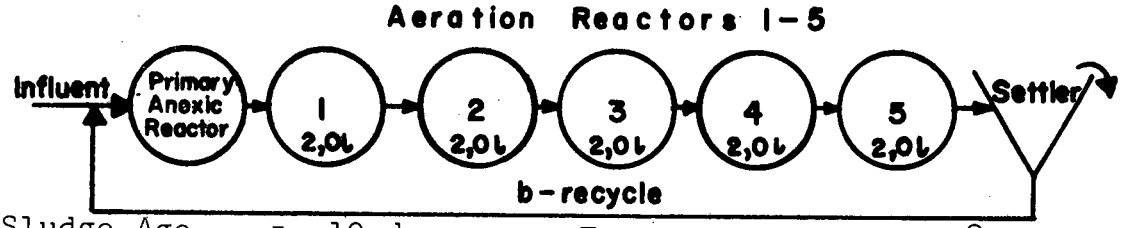


Fig. 9. Coefficient of phosphorus removal (dP/dS) for various actual anoxic retention times observed in a plug-flow primary anoxic reactor.

The data shown in Figs. 8 and 9 were obtained under conditions where the MLVSS and MLVASS (mixed liquor volatile active suspended solids) remained approximately constant. However, since the work of Shapiro et al[18] has indicated that the rate of release of phosphorus increases with increasing sludge mass, it is probable that the optimum actual anoxic retention time is a function of the MLVASS concentration in a particular system.

ACTUAL AERATION TIME REQUIRED FOR PHOSPHORUS REMOVAL.

Under batch test or plug-flow conditions, an actual aeration time of 2 - 4 hours, was reported to be required for maximal uptake of phosphorus[6,12]. In an attempt to determine the phosphorus uptake profile under non-ideal plug-flow conditions, an intermediate plug-flow aeration system with a return sludge recycle ratio of 2 was established (Fig. 10). This configuration consisted of an anoxic reactor followed by five aeration reactors in series. All the reactors were of equal volume, each having an actual retention time of twenty minutes. The process data are given in Fig. 10.



Sludge Age = 10 days Temperature = 20°C
Influent flow = 48 ℓ/d b recycle ratio = 2

Reactors	Nominal retention time (hrs)	Actual retention time (mins)
Primary anoxic	1,0	20
Aeration	1,0	20

Fig. 10. Intermediate plug-flow configuration with process data.

The results are shown in Table. 5. In particular, the removal of phosphorus from the system was 6,9 mg/ℓ total PO_4-P which is far in excess of that normally required for cell growth. With the short actual anoxic retention time of 20 minutes no phosphorus was released in the primary anoxic reactor (see Fig. 11). In fact the system removal of phosphorus must have occured in the primary anoxic reactor for there was no change in the phosphorus concentration as the flow passed through the system - yet removal had occured between influent and efluent. In this configuration therefore, the aeration time did not directly contribute to the phosphorus removal as it essentially all occured in the anoxic reactor.

Parameter (mean values)	Influent	Primary Anoxic	Aeration reactor 5
Total PO_4-P (mg/ℓ)	10,8	3,9	3,9
NO_3-N "		4,7	8,4
NO_2-N "		0,2	0,2
MLVSS "			2783
TKN "	32,8		16,8
COD "	379		37
Phosphorus removed = 6,9 mg/ℓ total PO_4-P			

Table 5. Data from intermediate plug-flow unit.

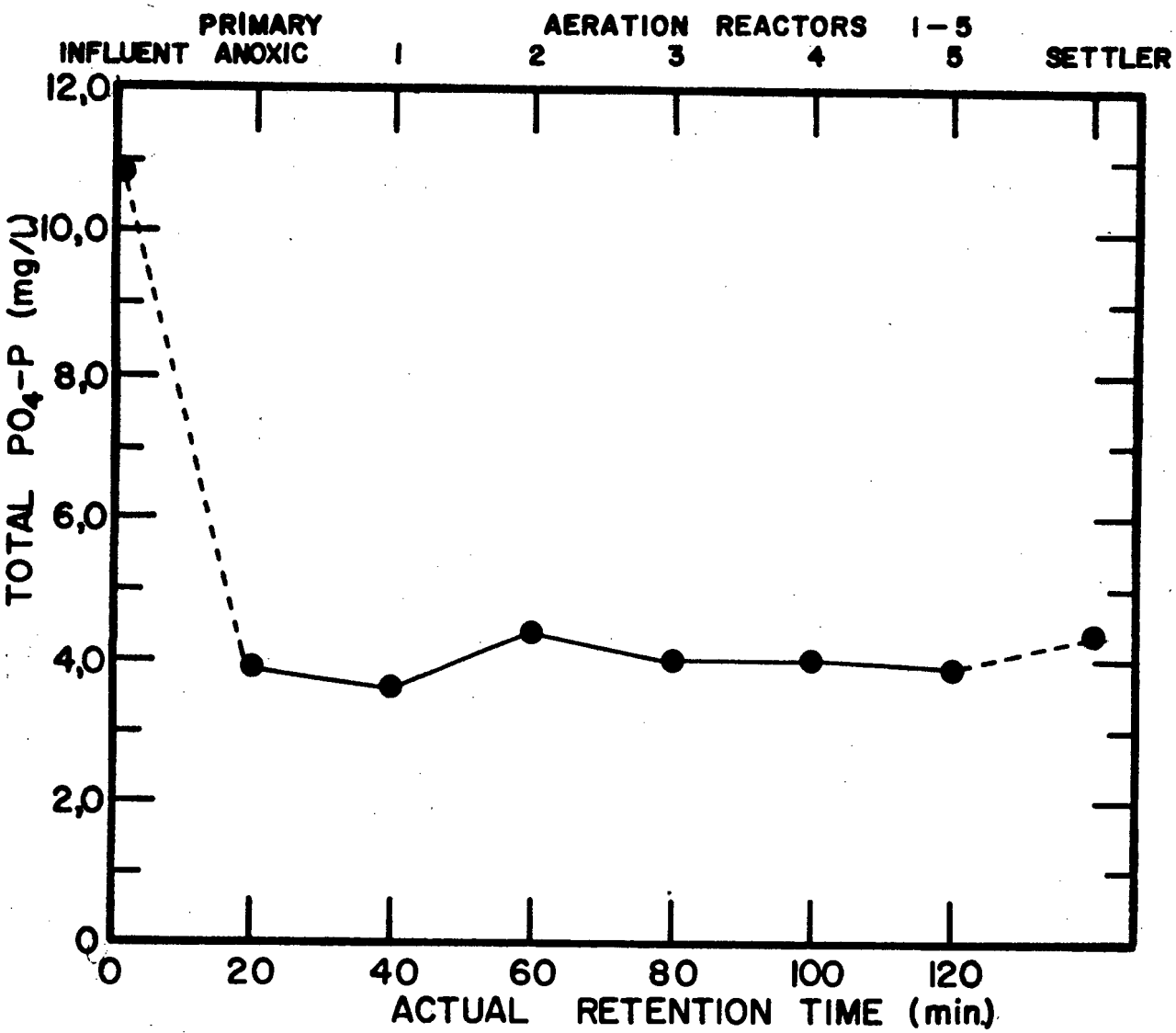


Fig. 11. Mean filtrate total PO_4-P values observed in an intermediate plug-flow system with a primary anoxic reactor.

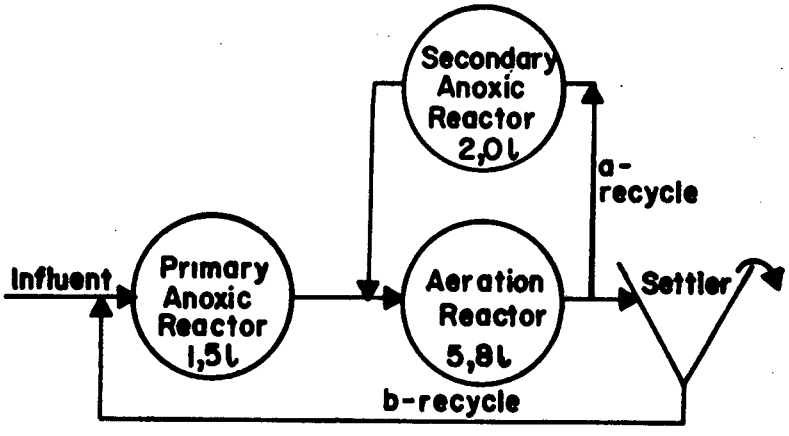
These data confirm the conclusions of Marsden[30] that for actual anoxic retention times of less than 30 minutes phosphorus is removed in the primary anoxic reactor. The data are also in agreement with those made on the configuration in Fig. 6.

This experiment therefore indicates that a long actual aerobic retention time is unnecessary and confirms the conclusion reached earlier that the actual aerobic retention time is not of significance in completely mixed and intermediate plug-flow systems. However, in activated sludge systems the nominal time will usually be much longer than the actual retention time and is fixed by the MLVSS concentration allowed in the reactor. Usually the nominal retention time will be so long (at sludge ages greater than 10 days and MLVSS concentrations of approximately 3000 mg/ℓ) that it is always likely to be sufficient for the plant behaviour. Consequently it was felt that at this stage investigation into aeration times was not profitable.

INFLUENCE OF NITRATES.

As discussed earlier Barnard[22] in his nitrification-denitrification system considers the elimination of nitrates to be an essential precondition for excess uptake of phosphorus. Barnard states that unless nitrates are reduced to near zero levels in the anoxic zones the required anaerobic condition will not be attained[23]. One may question the assertion that anaerobic conditions can only occur once nitrates are completely removed. Only a fraction of the organisms can use nitrate as a hydrogen ion acceptor so that irrespective of whether nitrates are present or not, a large fraction of the sludge micro-organisms are essentially anaerobic in his terms. However, according to him the presence of substantial amounts of nitrates in the anoxic reactors have an adverse effect on phosphorus removal.

This hypothesis was tested by running the configuration shown in Fig. 12 with the a recycle = 1 and b recycle = 2 under conditions where full denitrification occured in both anoxic reactors. Ammonium chloride was then added to the influent. This allowed the nitrate concentration in the unit to build up to such a level that full denitrification was not possible. The anoxic reactors were thus never "anaerobic". The configuration and process data are given in Fig. 12. The results are given in Table 6.



Sludge Age = 15 days Temperature = 20°C
Influent flow = 18,75 ℓ/d Recycle ratios: a=1 ; b=2

Reactors	Nominal retention time (hrs)	Actual retention time (mins)
Primary anoxic	1,92	38
Secondary anoxic	2,56	153
Aeration	7,52	113

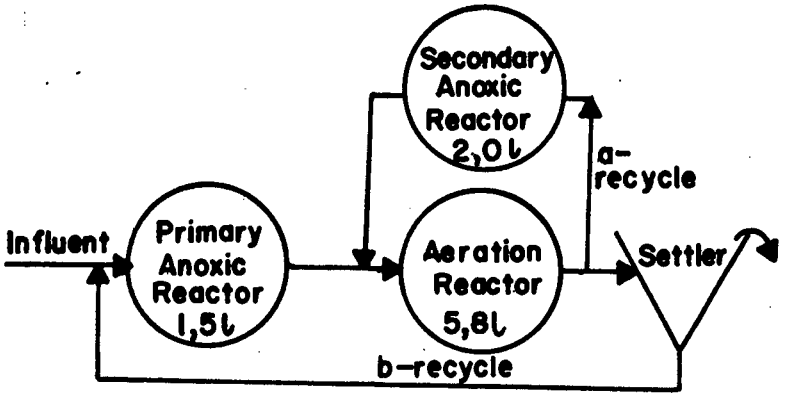
Fig. 12. Configuration and process data of unit used to test the effect of an increase in nitrate concentration on phosphorus removal.

Before NH_4Cl Addition				
Parameter (mean values)	Inf.	Primary Anoxic	Secondary Anoxic	Aeration/ Settler
Total PO_4-P(mg/ℓ)	17,4	9,2	6,5	6,0
NO_3-N "	<0,2	0,5	0,5	5,1
MLVSS "			3388	
TKN "	35,7		5,2	
COD "	663		32	
pH "		7,6	7,5	7,5
Phosphorus removed = 11,4 mg/ℓ total PO_4-P				
After NH_4Cl Addition				
Parameter (mean values)	Inf.	Primary Anoxic	Secondary Anoxic	Aeration/ Settler
Total PO_4-P(mg/ℓ)	20,2	8,0	8,5	7,2
NO_3-N "		11,2	7,3	17,3
MLVSS "				3878
TKN "	52,7			9,6
COD "	509			55
pH "		7,3	7,2	7,2
Phosphorus removed = 13,0 mg/ℓ total PO_4-P				

Table 6. Data from unit run with initial low nitrate concentrations and subsequent high nitrate concentration through addition of NH_4Cl.

Contrary to the hypothesis, an increase in phosphorus removal occured with the increase in anoxic zone nitrate concentration. It was not certain however that the increase was a direct result of the ammonium chloride addition. To confirm that the observed increase in phosphorus removal was due to NH_3Cl addition the configuration shown in Fig. 13 was run as follows:

Initially, by adding NH_3Cl, high nitrate concentrations were induced and thereafter the NH_3Cl feed was removed resulting in lower nitrate concentrations. This configuration did not give full denitrification even when no NH_3Cl was added. The results are given in Table 7.



Sludge Age = 15 days Temperature = 20°C
Influent feed = 18,75 ℓ/d Recycle ratio: a = 1; b = 4

Reactors	Nominal retention time (hrs)	Actual retention time (mins)
Primary anoxic	1,92	23
Secondary anoxic	2,56	153
Aeration	7,52	90

Fig. 13. Configuration and process data of unit used to test the effect of a decrease in nitrate concentration on phosphorus removal

With NH_4Cl Addition				
	Influent	Primary Anoxic	Secondary Anoxic	Aeration/ Settler
Total P (mg/ℓ)	20,2	8,9	6,7	7,0
NO_3-N "	0,3	13,6	17,7	23,3
MLVSS "				3263
TKN "	68,8			2,8
COD "	586			83
pH		7,5	7,4	7,4
Phosphorus removed = 13,2 mg/ℓ total PO_4-P				

With NH_4Cl Addition Stopped				
	Influent	Primary Anoxic	Secondary Anoxic	Aeration/ Settler
Total P (mg/ℓ)	13,1	6,1	5,8	5,0
NO_3-N "		6,0	4,4	9,9
MLVSS "				3177
TKN "	43			2,4
COD "	612			36
Phosphorus removed = 8,1 mg/ℓ total PO_4-P				

Table 7. Data from unit run with initial high nitrate concentrations through addition of NH_4Cl, and subsequently at low nitrate concentrations.

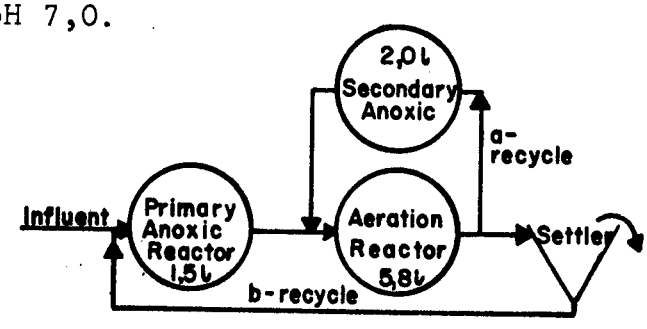
When the NH_4Cl addition was stopped, the phosphorus removal was found to decrease. The results confirm that the high nitrate concentration had no adverse influence on the phosphorus removal and that the higher NH_3Cl feed

in fact promoted phosphorus removal.

It was concluded that Barnard's hypothesis did not hold in this experiment, i.e. good phosphorus removal was not found to be dependent on anoxic zone nitrate concentrations. It is of interest to note that Vacker et al[14] observed that phosphorus removal was promoted sharply during the early stages of nitrate formation.

INFLUENCE OF pH

According to Levin and Shapiro[6] the optimum pH for biological removal of phosphorus is between pH 7-8. Under conditions where the influent waste waters are soft, poorly buffered, and nitrification occurs, the pH of the mixed liquor may fall considerably below this range. Even with denitrification the mixed liquor pH may fall below pH 7,0.



Sludge Age = 15 days Temperature = 20°C
Influent flow = 18,75 ℓ/d Recycle ratio: a=1 ; b=2

Reactors	Nominal retention time (hrs)	Actual retention time (mins)
Primary anoxic	1,92	38
Secondary anoxic	2,56	153
Aeration	7,52	113

Fig. 14. Configuration and process data of unit used to test effect of pH on phosphorus removal.

To investigate the pH effect, a unit with configuration shown in Fig. 14, was tested. The mixed liquor aeration reactor pH was 6,6. The pH was then raised to 7,5 by adding sodium bicarbonate to the influent. The results are given in Table 8.

Before $NaHCO_3$ Addition				
Parameter (mean values)	Inf.	Primary Anoxic	Secondary Anoxic	Aeration/ Settler
Total P (mg/ℓ)	14,8	9,9	6,0	8,7
NO_3-N "	0,2	1,5	4,1	8,5
MLVSS "				3355
TKN "	29,5			7,5
COD "	574			56
pH		6,8		6,6
Phosphorus removed = 6,1 mg/ℓ total PO_4-P				

After $NaHCO_3$ Addition				
	Inf.	Primary Anoxic	Secondary Anoxic	Aeration/ Settler
Total P (mg/ℓ)	16,6	12,5	10,1	8,5
NO_3-N "	0,2	0,5	7,7	8,3
MLVSS "				2857
TKN "	33,9			5,2
COD "	574			56
pH		7,5	7,5	7,5
Phosphorus removed = 8,1 mg/ℓ total PO_4-P				

Table 8. Data from unit used to test the effect of increased pH on phosphorus removal.

After raising the pH of the mixed liquor to pH 7,5 an increase in phosphorus removal from 6,1 mg/ℓ to 8,1 mg/ℓ

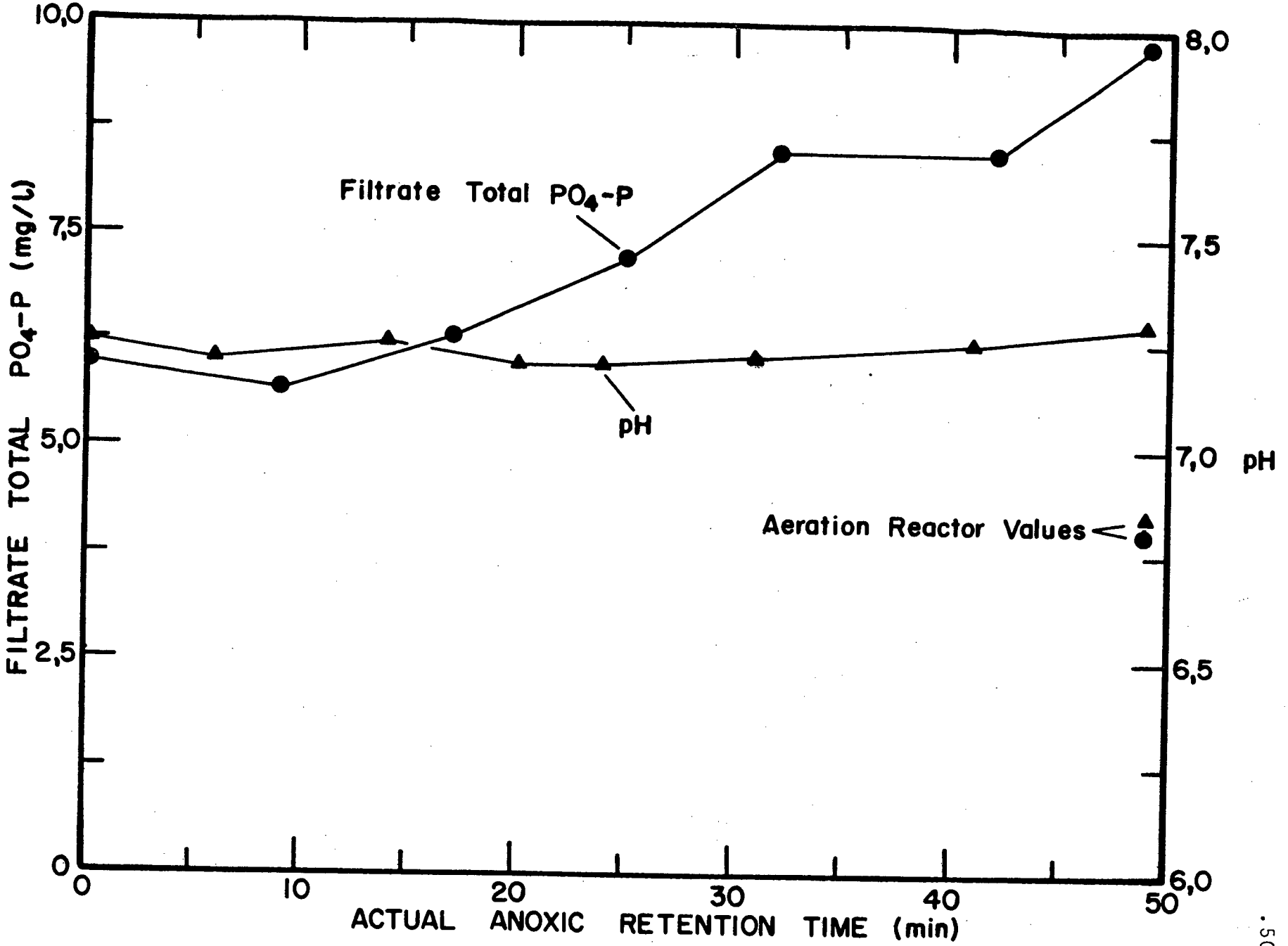


Fig. 15. Filtrate total PO_4-P and mixed liquor pH values through a plug-flow primary anoxic reactor.

total PO_4-P was observed. This suggests that pH may exert some influence on phosphorus removal. The possibility cannot be excluded that the addition of the monovalent cation, sodium, also enhanced the removal[8].

The increase in phosphorus removal with pH, observed above, is not due to the precipitation mechanism proposed by Menar and Jenkins[5]. This is evident from the soluble phosphorus and pH profiles through a plug-flow anoxic reactor (Fig. 15): Usually the pH drops in an anoxic reactor due to the accumulation of dissolved CO_2. But in an anoxic system where denitrification is taking place the pH may rise. Now, according to Menar and Jenkins[5], a rise in pH may result in cationic precipitation of phosphorus and thus remove soluble phosphorus from the liquid. However, from the profile in Fig15 it can be seen that although the pH increased the soluble phosphorus concentration also increased through the anoxic zone.

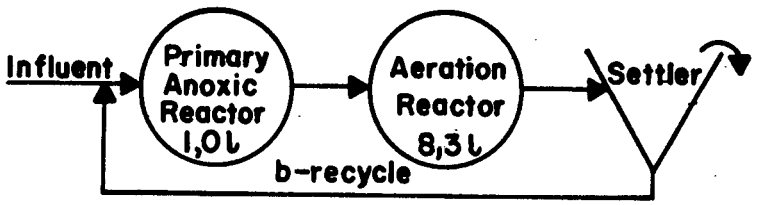
Menar and Jenkins[5] also stated that the resolubilization of phosphorus is due to the fall in pH in the anoxic zone - i.e. a purely chemical mechanism of resolubilisation. The experiment in Fig.15 indicates that release of phosphorus must be biological because the pH rose while resolubilisation of phosphorus occured in the anoxic reactor.

INFLUENT PHOSPHORUS CONCENTRATION

From the literature it is probable that if the uptake of phosphorus is an active transport mechanism, the dissolved phosphorus concentration will have no effect on the phosphorus uptake. Orthophosphate is the only form of phosphorus assimilated by the organisms. If a high fraction of influent phosphorus is not in the orthophosphate form, increased phosphorus uptake may be observed on the addition of orthophosphate. In Cape waters, ortho-

phosphate determinations cannot be made on the influent because of interference from organic compounds. Only total phosphorus tests were therefore used.

To examine the effect of high concentrations of dissolved orthophosphate, varying concentrations of potassium orthophosphate were added to the influent. The configuration and process data are given in Fig. 16. Results are given in Table 9.



Sludge Age = 15 days Temperature = 20°C
Influent flow = 18,75 ℓ/d b-recycle ratio = 2

Reactors	Nominal retention time (hrs)	Actual retneiton time (mins)
Primary anoxic	1,28	26
Aeration	10,62	212

Fig. 16. Configuration and process data of unit used to test the effect of influent phosphorus concentration on phosphorus removal.

There appears to be no relationship between the influent phosphate concentration and the concentration removed. The added monovalent cation had no effect on the phosphorus removal, as no additional phosphorus was taken up in any quantity. This experiment also indicates that most of the phosphorus in the influent must have been hydrolysed to the orthophosphate form, for the removal was not a function of the added orthophosphate.

No K_3PO_4 added			
Parameter (mean values)	Influent	Primary Anoxic	Aeration/ Settler
Total PO_4-P(mg/ℓ)	16,2	10,6	11,3
NO_3-N "		15,8	23,4
MLVSS "			3875
TKN "	47,4		3,1
COD "	-		-
Phosphorus removed = 4,9 mg/ℓ total PO_4-P			

K_3PO_4 added			
Parameter (mean values)	Influent	Primary Anoxic	Aeration/ Settler
Total PO_4-P(mg/ℓ)	28,7	19,4	19,6
NO_3-N "		8,2	15,6
MLVSS "			2804
TKN "	37,8		2,8
COD "	613		39
Phosphorus removed = 9,1 mg/ℓ total PO_4-P			

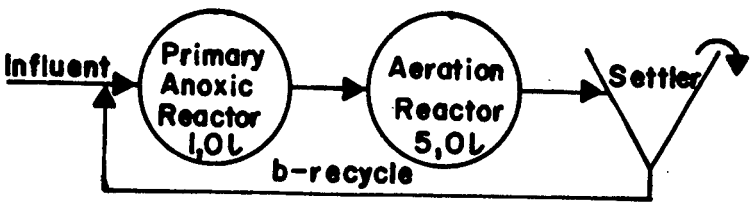
More K_3PO_4 added			
Parameter (mean values)	Influent	Primary Anoxic	Aeration/ Settler
Total PO_4-P(mg/ℓ)	34,2	23,4	27,3
NO_3-N "		10,0	18,8
MLVSS "			2155
TKN "	35,1		6,9
COD "	551		63
Phosphorus removed = 6,9 mg/ℓ total PO_4-P			

Table 9. Data from unit used to test the effect of influent phosphorus concentration on phosphorus removal

INFLUENCE OF COD

From the literature the role of the influent substrate concentration in the phosphorus removal process is not clear. Some investigators like Carberry and Tenney[8] state that the substrate concentration has little influence within the normal range found in activated sludge plants. In contrast, Sherrard and Schroeder[32] have presented a hypothesis based on cell growth rate and stoichiometry which predicts that the substrate concentration is of considerable influence. According to their theory the greater the mass of biodegradable COD available, the greater the mass of cells produced and the higher the phosphorus removal.

In order to determine whether the influent substrate concentration is of any significance in phosphorus removal, units exhibiting luxury uptake were run at three different influent COD concentrations. In all the units the sludge age was kept constant at 10 days. The configuration and process data are given in Fig. 17. The results are given in Table 10.



Sludge Age = various Temperature = 20^{0}C
Influent flow = 19 ℓ/d b-recycle ratio = 2

Reactors	Nominal retention time (hrs)	Actual retention time (mins)
Primary anoxic	1,26	25
Aeration	6,31	126

Fig. 17. Configuration and process data of units used to test effect of influent COD and sludge age on phosphorus removal.

Unit 1	Influent	Primary Anoxic	Aeration/ Settler
Total PO_4-P(mg/ℓ)	15,2	1,9	1,9
NO_3-N "		3,5	7,6
MLVSS "			5400
TKN "	45,8		8,2
COD "	557		63
pH		7,0	6,8
Phosphorus removed = 13,3 mg/ℓ total PO_4-P			
$\Delta P/\Delta COD$ = 0,0300			

Unit 2	Influent	Primary Anoxic	Aeration/ Settler
Total PO_4-P(mg/ℓ)	13,9	5,0	4,4
NO_3-N "		-	-
MLVSS "			5056
TKN "	43,2		13,8
COD "	453		51
pH		7,3	7,2
Phosphorus removed = 9,5 mg/ℓ total PO_4-P			
$\Delta P/\Delta COD$ = 0,0279			

Unit 3	Influent	Primary Anoxic	Aeration/ Settler
Total PO_4-P(mg/ℓ)	11,9	3,7	4,3
NO_3-N "		4,5	6,2
MLVSS "			2033
TKN "	31,5		5,0
COD "	342		41
pH		7,2	7,1
Phosphorus removed = 7,6 mg/ℓ total PO_4-P			
$\Delta P/\Delta COD$ = 0,0296			

Table 10. Data from identical units operated at 3 different influent COD concentrations to determine the effect of influent COD on phosphorus removal.

It is clear from the data that the influent COD concentration exerts a considerable influence on phosphorus removal. At different influent COD concentrations correspondingly different phosphorus concentrations were removed from the system. It is of significance however that the ratio of phosphorus removed to the biodegradable COD concentration removed ($\Delta P/\Delta$ COD) remained approximately constant under the three conditions imposed. These findings support the hypothesis proposed by Sherrard and Schroeder[32], although they do not assume a luxury uptake mechanism of phosphorus assimilation.

INFLUENCE OF SLUDGE AGE

The influence of sludge age in the phosphorus removal process does not appear to have been experimentally investigated. Kinetic theories of activated sludge[21] show that the phosphorus requirements for cell synthesis decrease with increased sludge age. Sherrard and Schroeder[32] also concluded that on the basis of cell growth rates and stoichiometry, reduced phosphorus removal at longer sludge ages is to be expected.

It is not known, however, how sludge age affects phosphorus removal under conditions where luxury uptake occurs. This aspect was investigated by operating one unit at 30 days sludge age and another identical unit at 10 days, keeping all other parameters constant. The configuration used and process data are given in Fig. 17. The results are given in Table 11.

10 day sludge age unit			
Parameter (mean values)	Influent	Primary Anoxic	Aeration/ Settler
Total PO_4-P(mg/ℓ)	14,6	3,0	2,9
NO_3-N "		2,7	5,1
MLVSS "			5284
TKN "	44,5		11,0
COD "	512		58
pH		7,1	7,1
Phosphorus removed = 11,6 mg/ℓ total PO_4-P			
$\Delta P/\Delta COD$ = 0,0298			

30 day sludge age unit			
Parameter (mean values)	Influent	Primary Anoxic	Aeration/ Settler
Total PO_4-P(mg/ℓ)	9,9	5,9	5,5
NO_3-N "		10,4	18,1
MLVSS "			4535
TKN "	32,9		4,5
COD "	435		37
pH			6,7
Phosphorus removed = 4,4 mg/ℓ total PO_4-P			
$\Delta P/\Delta COD$ = 0,0129			

Table 11. Data from two identical unit operated at different sludge ages to determine the effect of sludge age on phosphorus removal.

It is apparent that a significant increase in phosphorus removal can be achieved by decreasing the sludge age of the system. This means that the ratio phosphorus removed/COD utilised does not remain constant for different sludge ages.

PRELIMINARY CONCLUSIONS

While the preliminary experimental results reported above could be more positively verified, it was felt that sufficient information was given by the tests to form the following conclusions:-

1. "Luxury" uptake of phosphorus may be induced by the presence of an anoxic zone in the activated sludge process. The actual anoxic retention time exerts a profound influence on the mass of phosphorus removed.
2. If a primary and a secondary anoxic reactor are present in the system, the actual retention time of the primary anoxic reactor will have the dominant effect on phosphorus removal.
3. In a system where only a primary anoxic reactor is present, there is an optimum actual anoxic retention time for obtaining maximum phosphorus removal. This optimum value appears to coincide with the condition where there is no nett release of phosphorus into solution under anoxic conditions. Decreasing or increasing the actual retention time below or above the optimum value has a detrimental effect on phosphorus removal.
4. Anoxic stripping of phosphorus is not a prerequesite for luxury uptake of phosphorus to occur.
5. Increasing the influent ammonia-nitrogen and hence the reactor nitrate concentration enhances phosphorus removal.
6. An increase in aeration reactor pH to between pH 7-8 enhances phosphorus removal.
7. The mechanism of removal does not appear to be pre-

cipitation. Although an increase in pH through the anoxic reactor due to denitrification was observed, phosphorus was released into solution.

8. The degree of phosphorus removal is independent of the influent phosphorus concentration.
9. The mass of phosphorus removed appears to be directly linked to the influent COD utilised. The ratio of phosphorus removed to the COD utilised is constant at a particular sludge age. The higher the COD utilised, the greater the concentration of phosphorus removed.
10. The concentration of phosphorus removed appears to be a function of the sludge age. For a fixed influent COD the longer the sludge age the less phosphorus removed.

In summary: The factors which appear to have a major influence on phosphorus removal are:

(i) presence of a primary anoxic zone;
(ii) length of primary anoxic reactor actual retention time;
(iii) concentration of COD;
(iv) sludge age.

CHAPTER 3 KINETIC THEORY OF PHOSPHORUS REMOVAL

INTRODUCTION

The mass of phosphorus removed from the liquid can only leave the system via the sludge wastage per day. In the previous chapter the preliminary data indicated that for the same sludge age, as the biodegradable COD increased, phosphorus removal increased; and for the same COD feed, as the sludge age decreased phosphorus removal was found to increase. These observations led to the idea that perhaps the enhanced phosphorus removal is directly linked to the kinetic theory of the activated sludge process so that once conditions have been created favourable to inducing enhanced phosphorus removal, the magnitude of removal could be predicted. In formulating this hypothesis it was also considered that enhanced phosphorus uptake by the sludge occurs only through the action of the active sludge fraction, and that the endogenous and inert fractions are unlikely to have a phosphorus content greater than expected for organic material i.e. 2-3% w.r.t. VSS.

PROPOSED THEORY

Let X = a general parameter for sludge concentration in the reactor (mg/ℓ). Subscripts a, e, i and ii refer to active, endogenous, inert and inert influent respectively.

S_o = total influent COD (mg/ℓ)

S_i = biodegradable influent COD (mg/ℓ).

S = unmetabolized biodegradable COD in effluent (mg/ℓ)

Q = base flow (ℓ/d).

V = volume of reactor (ℓ).

R = hydraulic retention time (day) defined by V/Q.

R_s = sludge age (day) defined by $\frac{\text{mass of sludge in reactor}}{\text{mass of sludge wasted/d}}$

Y = growth yield coefficient - mass of organisms synthesized per mass of COD utilized (mg/ℓ).

b = endogenous mass loss rate constant (mg VAS/mg VAS/day).

P = concentration of phosphorus measured as total PO_4-P mg/ℓ .

ΔP = reduction in P in the influent total PO_4-P i.e. $(P_i - P)$

The letter M in front of a symbol indicates mass in mg, for example MX_a = mass of active sludge (mg);
Δ in front of a symbol indicates an increment in the parameter.

When sludge is generated in the activated sludge process, phosphorus is removed from the influent waste flow and incorporated in the sludge. Phosphorus can only leave the liquid via the sludge wasted per day i.e.:

Mass of P removed from influent = mass of P in sludge wastage i.e. then:

$$\Delta P.Q = \alpha MX/R_s \qquad (1)$$

where α is the fraction of phosphorus relative to the MLVSS

The sludge usually consists of three fractions - active, endogenous and volatile solids. Active and endogenous solids are generated by biological action. Inert volatile solids in the influent pass through the process without change. Eq. (1). can be rewritten as:

$$\Delta P.Q = (\alpha_1 MX_a + \alpha_2 MX_e + \alpha_3 MX_i)/R_s \qquad (2)$$

Assume that the fraction α in X_e and X_i is 0,03 and writing

$$\Delta P.Q = \left[\alpha MX_a + 0,03(MX_e + MX_i)\right] /R_s \qquad (3)$$

Marais and Ekama[32] have given the following relationships linking X_a and X_i with the biodegradable COD change, (S_i-S). At steady state:

$$MX_a = \frac{Y(S_i-S)Q.R_s}{1 + bR_s} \qquad (4)$$

$$MX_e = 0,2bR_sX_a = 0,2bR_s \left[\frac{Y(S_i-S)R_s.Q}{1 + bR_s}\right] \qquad (5)$$

$$MX_i = MX_{ii}R_s.Q$$

Furthermore X_{ii} can be written in terms of the influent COD S_o.

For unsettled municipal sewage

$$X_{ii} = (0,05 \text{ to } 0,09)S_o \tag{7}$$

i.e. $MX_{ii} = (0,05 \text{ to } 0,09)S_o.Q$

For settled sewage $X_{ii} = 0$.

Substitute Eqs. (4,5 and 7) in Eq. 3 and reducing

$$\Delta P = \frac{Y(S_i-S)}{1 + bR_s}\left[\alpha + 0,03 \times 0,2bR_s\right] + 0,09S_o \tag{8}$$

Eq. 7 can be modified further.

Now $S_i = S_o - S_{xii} - S_u$ (9)

hence $(S_i-S) = S_o - S_{xii} - S_u - S$

Now $S_{xii} = 1,42\ X_{ii} = 1,42 \times 0,09S_o$ (10)

$$S_u \approx 0,05S_o \tag{11}$$

S is negligible

$$\frac{(S_i-S)}{S_o} = \frac{(S_o-0,13.S_o-0,05.S_o)}{S_o} = 0,82 \tag{12}$$

$$(S_i-S) = 0,82S_o$$

$$S_o = \frac{S_i-S}{0,82} \tag{13}$$

i.e. $$\Delta P = \frac{Y(S_i-S)}{1 + bR_s}\left[\alpha + 0,03(0,2\ bR_s + \frac{1}{0,82})\right] \tag{14}$$

and $$\frac{\Delta P}{\Delta S} = \frac{P_i-P}{(S_i-S)} = \frac{Y}{1+bR_s}\left[\alpha + 0,03(0,2bR_s + \frac{1}{0,82})\right] \tag{15}$$

Eq.15 indicates that the removal of phosphorus concentration from the influent is a function principally of the removal of the biodegradable COD and the sludge age. The relationship provides a means for determining α. Under conditions where no luxury uptake of phosphorus occurs, α = 0,02 to 0,03. With this value the sludge age and influent biodegradable COD will have an insignificant effect on the phosphorus removal (Fig.18). However, under conditions where luxury uptake occurs, the value will be far higher and the sludge age and influent biodegradable COD become of great significance.

The hypothesis was tested by operating identical activated sludge units at different sludge ages and COD loadings. The sludge ages were maintained by withdrawing sludge twice a day. The configuration and process data are given in Fig.17. The actual anoxic retention time was set at approximately the optimum value of 30 minutes found earlier. The recycle ratio was kept constant at 2. The results should therefore show near optimum removal of phosphorus at the particular sludge age and COD loading.

1) The results are given in Table 12 and Figs. 18,19, and 20. While the scatter of data points is large, the trend predicted by the theory is apparent. The mean values of the coefficient dP/dS at sludge ages varying from 10-30 days all fall around the line representing α = 0,20 in Eq. 15 (Figs. 18 and 20)

When the sludge age was reduced from 10 days to 5 days the phosphorus removal significantly declined whereas theoretically it should have increased to very high values. It was not certain whether the process of phosphorus removal had ceased to function due to different phenomena becoming predominant or that the precipitous change in sludge age to half the former value was too great. It has been noted by Milbury et al[17],

Sludge Age (days)	Phosphorus mg/ℓ total PO_4-P			COD mg/ℓ		TKN mg/ℓ		pH		MLVSS mg/ℓ	NO_3+NO_2 mg/ℓ		
	Inf.	Prim. Anox.	Aeration/ Settler	Inf.	Aer./ Set.	Inf.	Aer./ Set.	Prim. Anox.	Aer./ Set.	Aer./ Set.	Prim. Anox.	Aer./ Set.	ΔP/ΔCOD
5	15,0	8,8	8,9	553	47	28,8	3,0	7,3	7,3	3312	1,7	11,7	0,0144
7	17,0	9,1	9,3	553	51	39,8	3,0	6,9	6,9	2779	8,0	15,7	0,0189
8	13,6	5,8	5,1	598	51	38,8	4,2	7,1	6,8	2555	9,2	16,1	0,0183
9	13,7	6,6	8,7	578	43	39,3	5,9	7,0	6,8	3875	5,2	12,8	0,0126
10	14,6	3,0	2,9	512	58	44,5	11,0	7,1	7,1	5284	2,7	5,1	0,0298
12	18,3	4,8	7,3	601	43	35,7	4,3	-	6,7	2704	7,9	12,9	0,0229
15	16,6	5,5	6,0	531	56	50,1	7,4	7,1	6,7	5172	5,3	14,4	0,0254
20	9,6	-	2,1	542	50	32,8	4,7	-	-	4222	-	-	0,0177
25	8,6	3,8	4,4	395	33	25,0	4,2	-	6,9	3859	6,7	12,6	0,0132
30	9,9	5,9	5,5	435	37	32,9	4,5	-	6,7	4535	10,4	18,1	0,0129

Table.12. Data from identical units operated at various sludge ages and influent COD concentrations

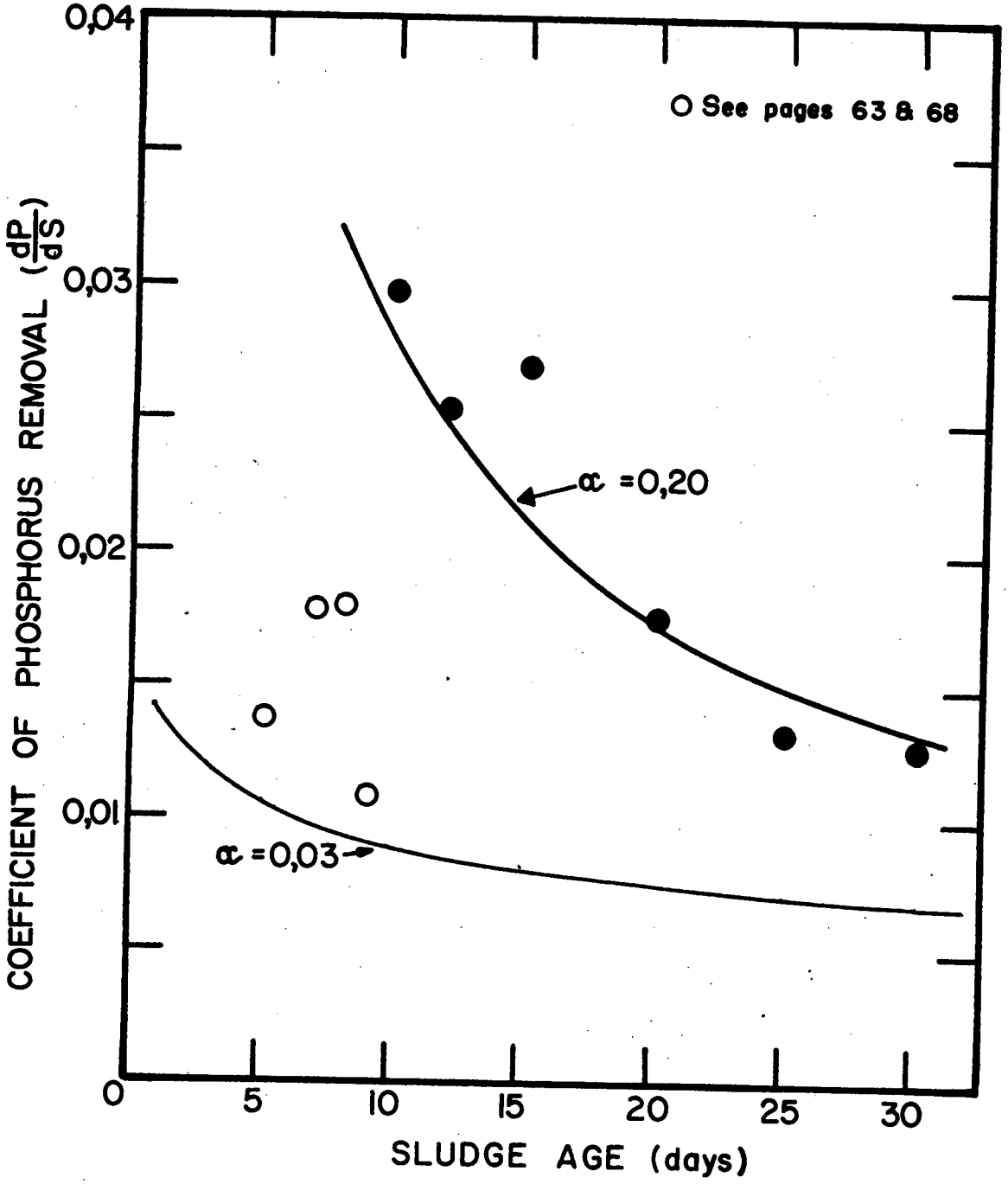


Fig. 18. Mean values of the coefficient of phosphorus removal (dP/dS) for identical units operated at different sludge ages.

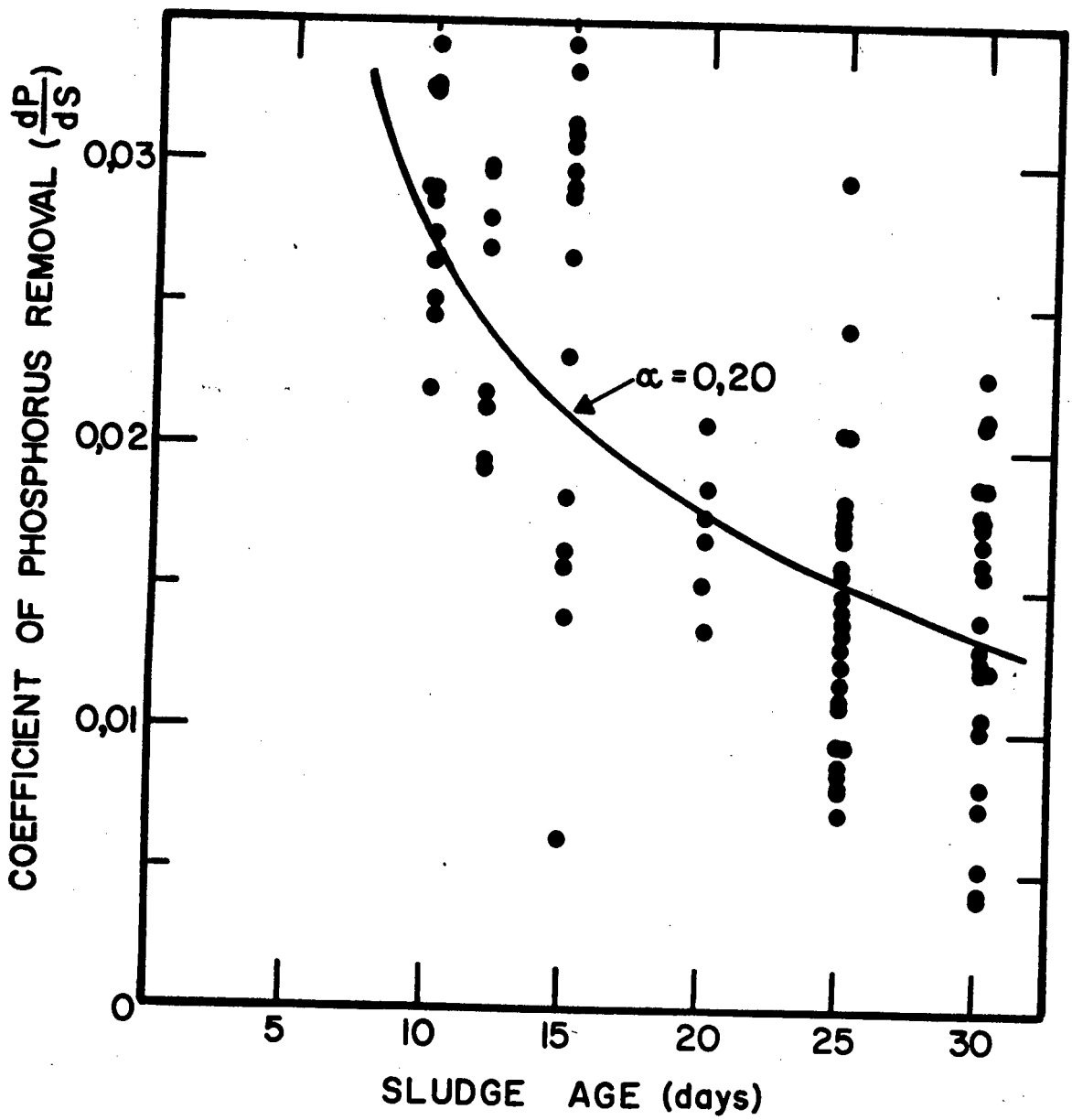


Fig. 19. Individual values for the coefficient of phosphorus removal (dP/dS) obtained at various sludge ages.

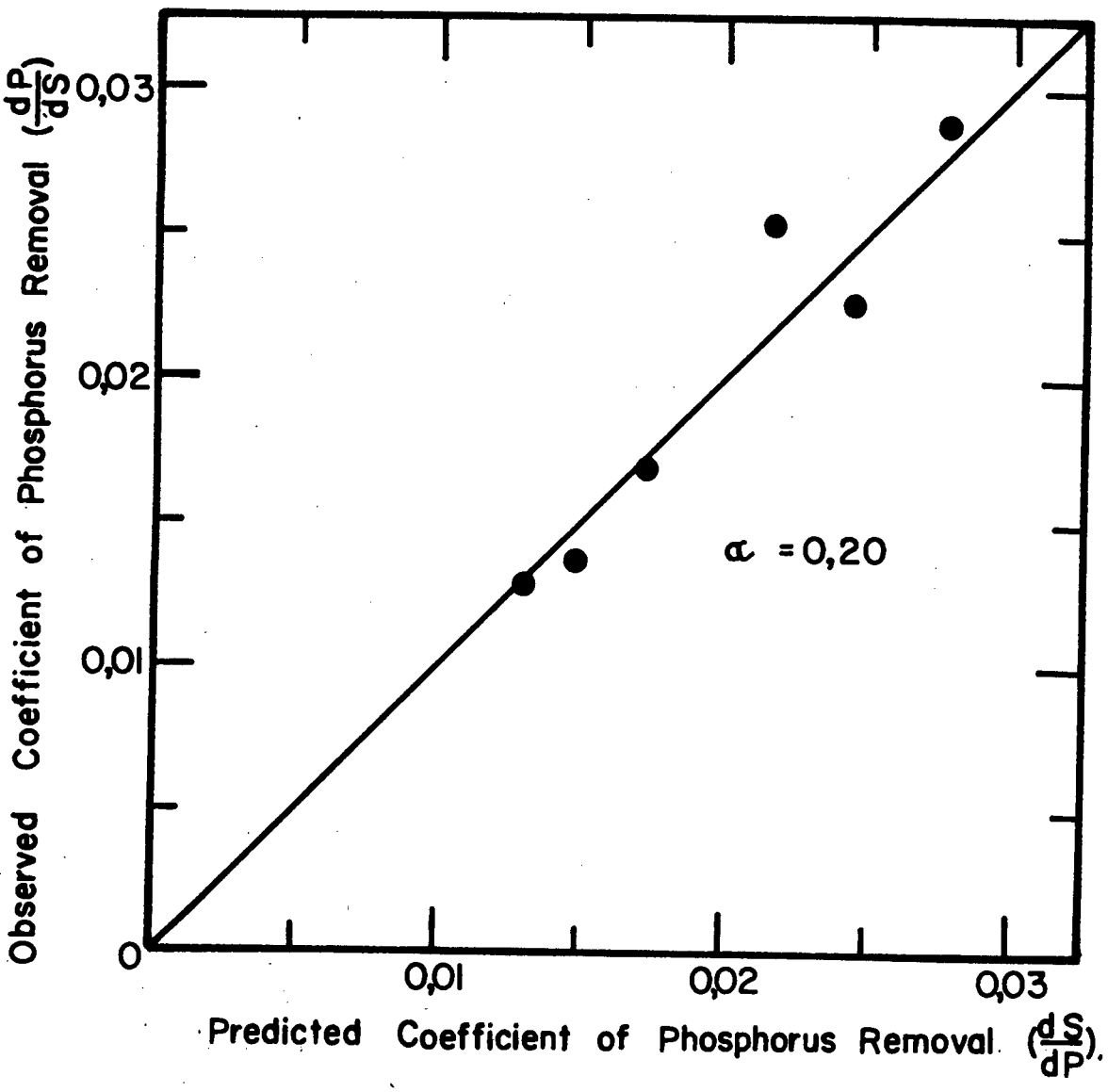


Fig. 20. Comparison of predicted vs. observed coefficient of phosphorus removal (dP/dS).

that a sudden increase in the rate of sludge wastage had an adverse affect on high phosphorus removal. In their study, one week was required before the high phosphorus removal was again achieved. It was reasoned that if the great change in sludge age was the cause, then in time the process would recover. However, after 3 sludge ages - 15 days - had passed no improvement was discernible. It was therefore concluded that either some functional change had occured in the removal mechanism or that a condition in the process as yet unknown had the adverse effect observed.

In order to determine if there was some minimum sludge age below which the process phosphorus removal process broke down, the sludge age was progressively increased to 7,8,9 and 12 days sludge age. The process was allowed to stabalise for longer than one sludge age after each increment. No significant improvement in phosphorus removal occured even when the 12 day sludge age was imposed. The process now gave far lower results than those formely obtained at a sludge age of 15 days. Possible some other condition - as yet unknown - was causing the process to break down. A chance change in the process gave a clue: The influent was directed into the aerobic reactor and not the anoxic reactor as previously. This almost immediately re-established the predicted values of phosphorus removal. (See Fig.21). The new mode of feed was continued for approximately one sludge age and showed consistently high removal. Reverting back to feeding into the anoxic reactor now maintained the high phosphorus removal. No rational explanation can be advanced for the behaviour observed. This behaviour should be investigated thoroughly as its elucidation may provide important clues to the phosphorus removal mechanism. Such an investigation would be particularly relevant, for in the literature efficient phosphorus removed has been obtained at short sludge ages[14].

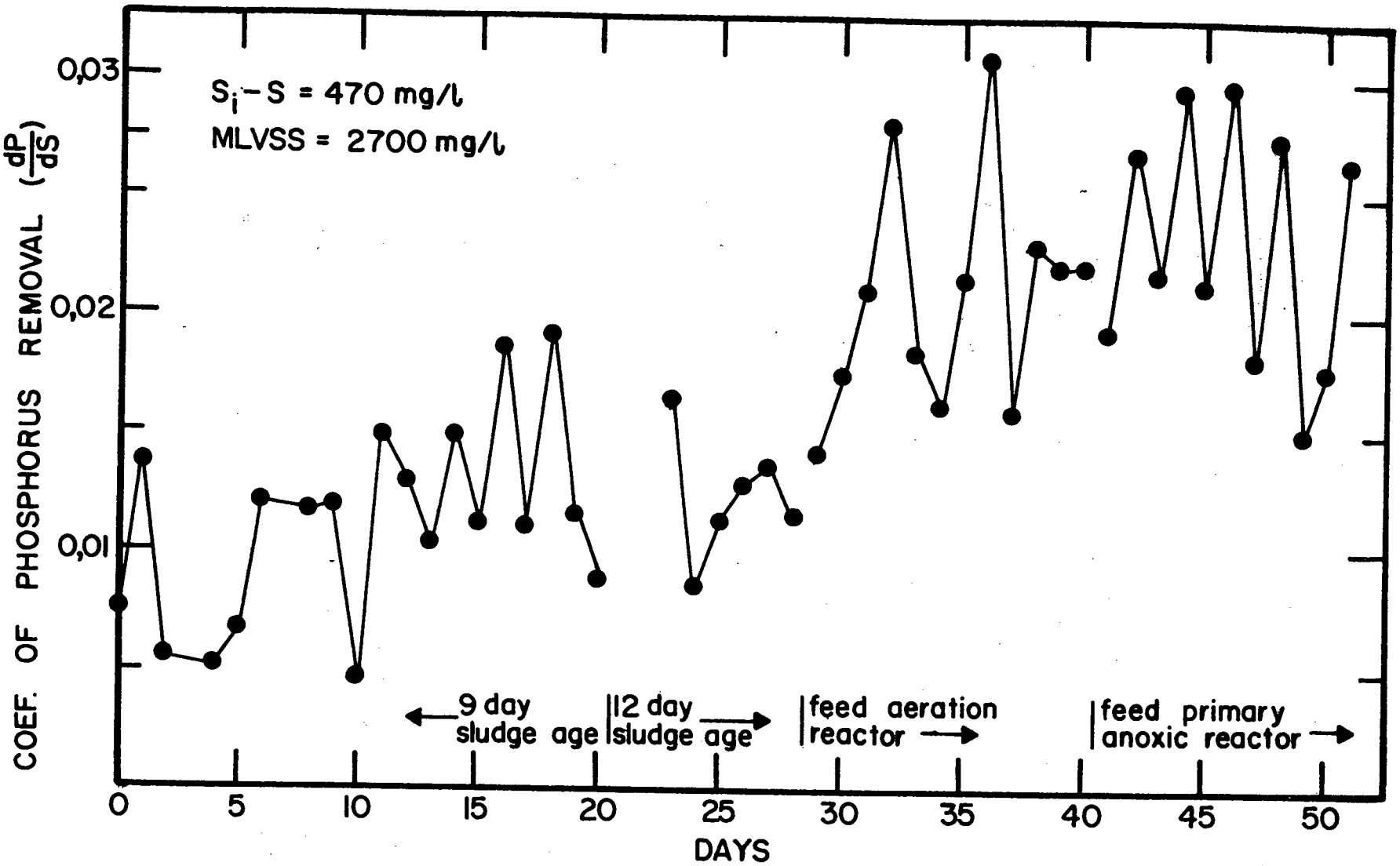


Fig. 21. Behaviour of a 12 day sludge age unit, showing initially poor phosphorus removal, when the influent feed was directed into the aeration reactor.

IRON CHLORIDE ADDITION

Towards the end of this investigation, Dr. L.J.R. van Vuuren of the National Institute for Water Research informed the writer of the phosphorus removal behaviour of an Infilco activated sludge plant at Scottburgh, Natal.

Prior to any coagulant addition, there was no detectable phosphorus removal in the plant. On subsequent coagulant addition into the aeration basin using aluminium sulphate, ferrous sulphate and ferric chloride, phosphorus removals, in the order of 5,3; 6,9 and 4,6 mg/ℓ PO_4-P were achieved for the three coagulants respectively[28]. Alum was dosed manually, while the results quoted for ferrous sulphate and ferric chloride were obtained under automated dosing conditions. Intermittently throughout the investigation, coagulant addition was terminated for periods ranging from 1 to 2 weeks. During these periods it was found that phosphorus removal, although considerably diminished, (approximately 1,9 mg/ℓ PO_4-P) still occured. It is not clear whether the continued removal was due merely to a biological mechanism or was a consequence of a build-up of chemicals in the reactor.

McClaren[33] reported that sludge from a Bardenpho plant giving reasonable phosphorus removal without coagulant addition contained a higher concentration of iron than would normally be expected. The above observations led to the hypothesis that increasing the metal concentration of the sludge would assist in inducing enhanced removal of phosphorus in the system.

To test this hypothesis 10 mg $FeCl_3$ per litre of influent was fed into the anoxic reactor of a 25 day sludge age unit (Fig. 17). Before iron addition the unit consistently removed phosphorus as predicted by the kinetic theory (i.e. $\Delta P / \Delta COD = 0{,}0132$). From an assumed Fe : P ratio of 1:1,

the added $FeCl_3$ was calculated to remove an additional 1,9 mg/ℓ P.

The results plotted in Fig 22 show that initially a mean concentration of approximately 4 mg/ℓ total PO_4-P was being removed. After $FeCl_3$ addition commenced there was a pronounced increase in the concentration removed to a level of approximately 7,5 mg/ℓ total PO_4-P. This high level of removal continued even when the $FeCl_3$ addition was stopped for a period. It is important to note that the additional concentration of phosphorus removed during the $FeCl_3$ feed is greater than can be predicted from the stoichiometric assumptions. The ratio of Fe:P was approximately 0,57:1 whereas Coetzee et al[28] found a ratio of 1,55:1 was required for optimum phosphorus removal. The concentration removed also showed less fluctuation than prior to the $FeCl_3$ addition.

From these preliminary observations it would appear that the addition of a metal salt (e.g. Fe or Al) may further enhance the luxury uptake of phosphorus. This may be of considerable importance in activated sludge plants where consistently low effluent concentrations are required and the phenomenon merits further investigation.

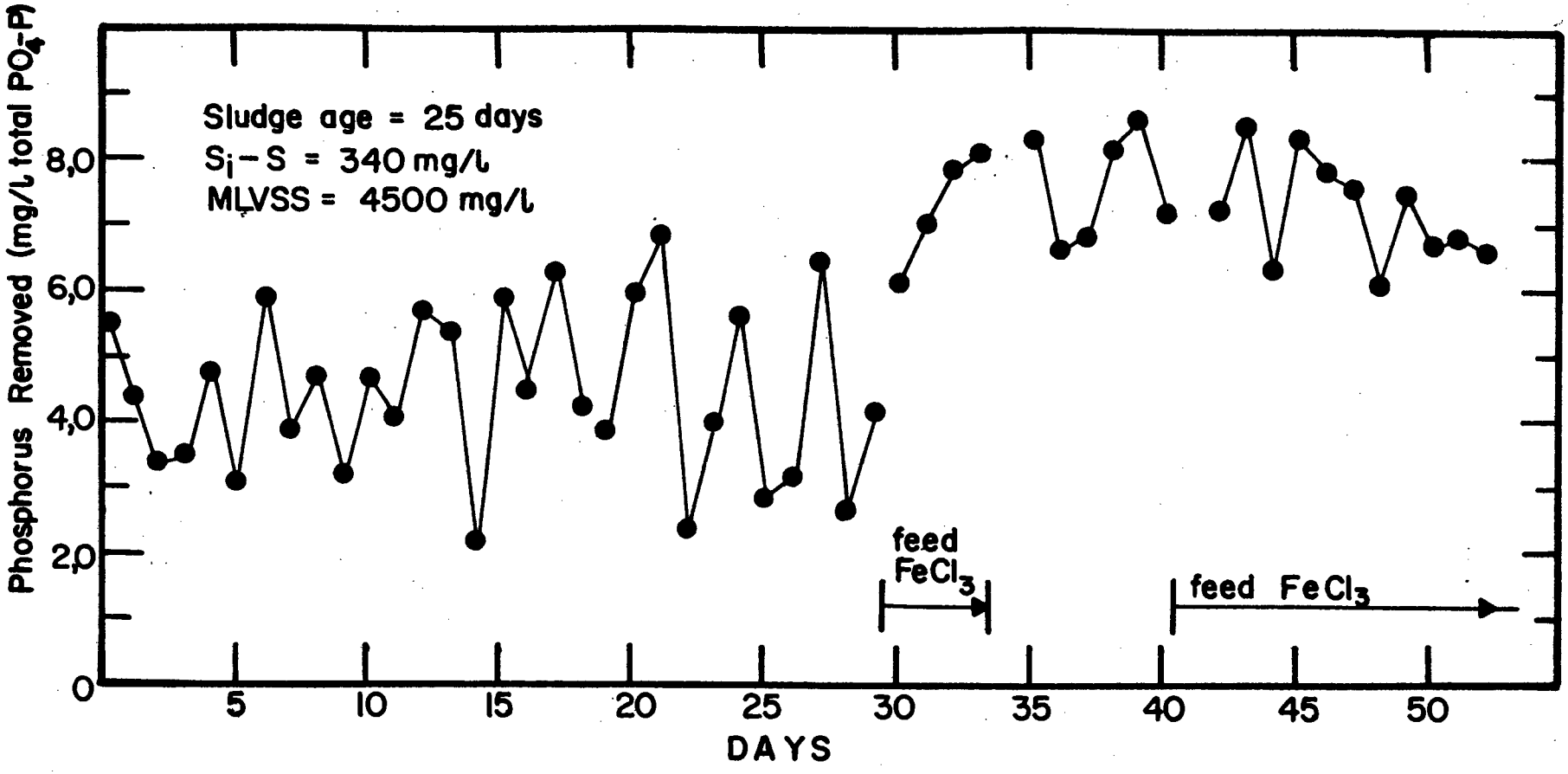


Fig. 22. Behaviour of a 25 day sludge age unit when 10 mg $FeCl_3$ per litre influent was fed into the primary anoxic reactor.

FINAL CONCLUSIONS

An investigation into the removal of phosphorus in the activated sludge process showed that: (1) Luxury uptake of phosphorus may be induced by the presence of an anoxic zone.

(2) If a primary and secondary anoxic reactor are present in the system, the actual retention time of the primary anoxic reactor will have the dominant effect on the degree of phosphorus removal.

(3) In a system where only a primary anoxic reactor is present, there is an optimum actual anoxic retention time for obtaining maximum phosphorus removal. This optimum value appears to coincide with the condition where there is no nett release of phosphorus in the anoxic zone. Decreasing or increasing the actual anoxic retention time either side of the optimum value has a detrimental effect on phosphorus removal.

(4) Increasing the influent ammonia - nitrogen and hence the reactor nitrate concentration, enhances phosphorus removal.

(5) An increase in aeration reactor pH to between pH 7-8 enhances phosphorus removal.

(6) The mechanism of removal does not appear to be precipitation. Although an increase in pH through the anoxic reactor was observed due to denitrification, phosphorus was released into solution.

(7) The degree of phosphorus removal is independent of the influent phosphorus concentration.

(8) Anoxic stripping of phosphorus is not a pre-requisite for luxury uptake of phosphorus to occur.

(9) The concentration of phosphorus removed is a function of the COD

utilized. The ratio of phosphorus removed to the COD utilized is constant at a particular sludge age, so that as the concentration of COD utilized increases the concentration of phosphorus removed increases.

(10) The concentration of phosphorus removed is a function of the sludge age. For a fixed biodegradable influent COD, the longer the sludge age, the less phosphorus removed.

In a configuration where the actual anoxic retention time is fixed, the concentration of phosphorus removed from the effluent may be described by the equation:

$$\Delta P = \frac{Y(S_i - S)}{1 + bR_s}\left[\alpha + 0{,}03(0{,}2bR_s + \frac{1}{0{,}82})\right]$$

Where: ΔP = reduction in phosphorus in the influent total PO_4-P i.e. ($P_{influent} - P_{effluent}$)

S_i = biodegradable influent COD (mg/ℓ)

S = unmetabolized biodegradable COD in effluent (mg/ℓ)

R_s = sludge age (day) defined by $\frac{\text{mass of sludge in reactor}}{\text{mass of sludge wasted/d}}$

Y = growth yield coefficient - mass of organisms synthesized per mass of COD utilized (mg/ℓ)

b = endogenous mass loss rate constant (mg VAS/mg VAS/day).

α = the fraction of phosphorus relative to the mixed liquor volatile active suspended solids (MLVASS).

Preliminary investigations into iron chloride addition indicates that iron appears to have disproportionately favourable effect on phosphorus removal under conditions where luxury uptake is taking place.

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APPENDIX I

DETERMINATION OF TOTAL PHOSPHATE - PHOSPHORUS USING COLORIMETRIC MOLYBDATE-VANADATE TECHNIQUE

Principle of the Method

In the presence of vanadates, phosphates react with molybdates to form yellow phosphovanadomolybdate. The intensity of this yellow colour, which is proportional to the amount of phosphate present is determined by absorbance using the spectrophotometer. This system obeys BEER'S LAW at a wavelength of 470µ to a concentration of 300 mg/ℓ.

If the sample is coloured by the presence of organic matter, this is removed by the addition of Anhydrous Sodium Carbonate and ashing.

Reagents

1. ANHYDROUS SODIUM CARBONATE: (Check the bottle as to the percentage impurity. That for phosphate should not exceed 0,001%. This quantity is negligible.)

2. VANADOMOLYBDATE REAGENT.

   Solution A: 20 g of ammonium molybdate tetrahydrate dissolved in 250 ml distilled water

   Solution B: 1 g ammonium metavanadate dissolved in 40 ml nitric acid (conc.) and 200 ml distilled water.

   Mix solutions A and B, add 100 ml nitric acid and dilute to 1 000 ml with water (stable for ± 12 months).

3. Solution C: 1 : 1 HNO_3 solution.

Technique

1. The sample is centrifuged or filtered using a Buchner funnel.

2. 25 ml of the sample is measured into a platinum bowl and boiled to dryness (see diagram for method of setting up apparatus). Takes $\pm$ 45 minutes.

3. Add $\pm$ 1 g Anhydrous Sodium Carbonate into the platinum bowl. Heat the Na_2CO_3 in the bowl strongly over a Meaker Bunsen for $\pm$ 10-15 minutes. The Na_2CO_3 melts. Using tongs, turn the bowl while heating in the flame to ensure that the Na_2CO_3 comes into contact with all the dried sample.
   Remove from flame, cool, wash bowl with 1-2 ml distilled water, pouring contents into a 25 ml volumetric flask.

4. Add Solution C dropwise to the platinum bowl till effervescence ceases. Transfer this solution to the 25 ml volumetric flask by rinsing bowl with distilled water. Add more HNO_3 to the platinum bowl to ensure complete dissolution of the PO_4-P into the HNO_3 solution and rinse again into the 25 ml volumetric flask. This procedure of adding HNO_3 solution and rinsing with distilled water should be repeated 3 times. Not more than 10 mls HNO_3 is usually required.

5. Make up volume to 25 ml.

6. Into a test tube add 5 ml treated sample and 5 ml Vanadomolybdate reagent. Stand for 10 minutes for colour to develop and read at λ = 470 μ

   (Note: It was found by experiment that colour did not fade even after standing for 24 hours).

   A blank is done using 5 ml distilled water plus 5 ml Vanadomolybdate reagent.